THE PREPARATION AND PROPERTIES OF TUNGSTEN HEXAFLUORIDE DERIVATIVES

by

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This thesis describes the original work of the author, except where specific references are given to the work of others. The present work was carried out in the Chemistry Department of the University of Glasgow between October 1966 and September 1969.

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ABSTRACT

The original aim of this investigation of the virtually unexplored chemistry of tungsten hexafluoride, WF_6, was to assess its usefulness as a fluorinating agent towards organic compounds. It is shown that WF_6 is a mild, selective fluorinating agent, limited in its applications. The work includes a study of the properties of derivatives of WF_6, and ^{19}F nuclear magnetic resonance spectroscopy has been used extensively.

A Raman spectroscopic study of the coloured solutions of WF_6 in the donor solvents benzene and acetonitrile indicates that the octahedral symmetry of WF_6 is preserved and that the extent of donor-acceptor interaction is small. Nitromethane was found to be a convenient solvent for the preparation of the complex fluorides $R_4N^+WF_6^-$ (R = ^nBu, ^nPr) by reaction of WF_6 with the appropriate tetraalkyl ammonium iodide. Attempts to isolate a solid donor-acceptor complex of WF_6 with a polycyclic aromatic hydrocarbon were unsuccessful.

Oxotetrafluoro(dimethyl ether)tungsten(VI), $WOF_4.OMe_2$, was obtained in good yield from the reaction of WF_6 with dimethyl ether under forcing conditions, and it is formulated as a monomeric, octahedral complex on the basis of its spectroscopic properties. The analogous complex $WOF_4.OEt_2$ decomposes readily. The interaction of WF_6 with thioethers and selenoethers has been studied, and the complexes

$WF_6(Et_2S)_2$ and $WF_6(Et_2Se)_2$ have been characterised. ^{19}F n.m.r. evidence has been obtained for the formation of the dimeric fluorine-bridged anion $W_2O_2F_9^-$ as a hydrolysis product of WF_6 derivatives.

The fluorination of some oxygen-containing compounds of sulphur and phosphorus by WF_6 has been studied. The reaction of WF_6 with dimethyl sulphoxide is complicated by the formation of HF, and one of the products is formulated as bis(monofluoromethyl)ether. WF_6 undergoes substituent-exchange reactions with sulphite esters to yield alkoxy and phenoxy tungsten(VI) pentafluorides, WF_5OR, (R=Me, Et, Ph) and fluorosulphite esters, ROS(O)F. The properties of these products are described. Pyrosulphuryl fluoride, $S_2O_5F_2$, is formed in the reaction of WF_6 with sulphur trioxide. The reaction of WF_6 with trimethyl phosphite gives initially WF_5OMe and $PF(OMe)_2$, but subsequent reactions occur to give $(MeO)_2P(O)Me$, $MeP(O)(F)OMe$, $(MeO)_3PMe^+WOF_5^-$ and $WOF_4.OP(OMe)_2Me$. The products obtained depend on the reaction conditions. PF_3 is formed in the reaction of WF_6 with dimethyl phosphite, and WF_5OMe, $WOF_4.OP(OMe)_2Me$ and $MeP(O)(F)OMe$ are the products of the reaction of WF_6 with $(MeO)_2P(O)Me$. The reactions of WF_5OMe with dimethyl sulphite, trimethyl phosphite, benzene, pyridine and dialkyl ethers are described.

The fluorination of methylalkoxysilanes and trimethylphenoxysilane with WF_6 has yielded a series of methoxy and phenoxy tungsten(VI) fluorides, $WF_{6-n}(OR)_n$, n = 1-4 (Me), n = 1, 2 (Ph), and some evidence

for the formation of $WF_4(OEt)_2$ and $WF_3(OPh)_3$ has been obtained. ^{19}F n.m.r. spectra indicate that these compounds are monomeric in solution, and geometrical isomers have been distinguished in some cases. The ^{19}F resonances are all to high field of WF_6, and the effects of OMe and OPh substituents on the chemical shifts are approximately additive. $WF_4(OMe)_2$ isomerises to $WOF_4.OMe_2$, and thermal decompositions of methoxy tungsten(VI) fluorides yield Me_2O or MeF with some reduction of the tungsten. WOF_4 is formed in low yield in the reaction of WF_6 with hexamethyldisiloxane; the other products are Me_3SiF and reduced tungsten species. Cleavage of the Si-N bond in dimethylaminotrimethylsilane with WF_6 was observed, but dimethylamino derivatives of WF_6 were not isolated.

Some of the factors which may determine the ^{19}F chemical shifts and stereochemistry of the tungsten fluoro-complexes prepared in this work are discussed. The ^{183}W chemical shifts of some of the complexes have been obtained by heteronuclear magnetic double resonance techniques, and these are all to low field of WF_6.

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INTRODUCTION

It is widely recognised that the last two decades have witnessed a renaissance in Inorganic Chemistry, and not least among the many expanding fields of study is the chemistry of fluorine and its compounds. Fluorine has been long recognised as the most reactive of the elements, combining with almost all the others, usually at moderate temperatures and with great vigour. The high reactivity of fluorine and the attendant difficulties of handling delayed a systematic study of its chemistry for many years. However, the demands of the nuclear programme towards the end of the Second World War and, more recently, the search for efficient rocket fuel oxidants have provided the impetus for a thorough and systematic study of the chemistry of fluorine and its compounds. The advent of the medium-temperature electrolytic cell for the production of fluorine on a laboratory scale, the development of suitable corrosion-resistant materials for the construction of apparatus, and the increasing commercial availability of many fluorine compounds have greatly reduced the experimental difficulties. The field affords many interesting and stimulating research problems, and the great effort which has been channelled into it has been rewarded by the discovery of a wide variety of

useful fluorine-containing compounds with properties ranging from the extreme fluorinating power of some binary fluorides to the almost complete inertness of perfluorinated-polymers.

The high reactivity of fluorine is undoubtedly associated with the low dissociation energy of the F_2 molecule. The most recent determination, by photoionisation methods, gives a value of 30.9 ± 0.7 kcal/mole.[1] Previous determinations gave values around 37 kcal/mole. The dissociation energies of the other halogens are: Cl_2, 58.2; Br_2, 46.1; I_2, 36.1 kcal/mole.[2] Repulsion between non-bonding electrons and the absence of suitable d-orbitals for multiple bonding have been forwarded as explanations for the weakness of the bond in F_2.

Fluorine is the most electronegative of the elements, and its high ionisation potential precludes the possibility of positive oxidation states. The fluorine compounds of the elements are of two main types, ionic and covalent, in all of which fluorine has a complete octet. Ionic fluorides contain the F^- ion, and in the numerous covalent fluorides the bonds have considerable ionic character as a result of the high electronegativity of fluorine. The coordination number of fluorine in covalent fluorides is usually one, but an increasing number of compounds are being shown to contain bridging fluorine atoms (e.g. refs. 3, 4). It is also currently suggested that the filled 2p orbitals of fluorine can engage in

π-bonding where suitable orbitals exist in the heteroatom (e.g. refs. 5, 6), but in most cases the evidence is largely circumstantial.

Fluorine-19 is the only naturally-occurring isotope of the element. It has a nuclear spin of $\frac{1}{2}$, and is an ideal nucleus for nuclear magnetic resonance (n.m.r.) spectroscopic investigations, as it has a favorable spin-lattice relaxation time and a gyromagnetic ratio close to that of the hydrogen nucleus. The ranges of ^{19}F chemical shifts and coupling constants are large compared with those obtained from ^{1}H n.m.r. spectra, and first-order ^{19}F n.m.r. spectra, which yield much information about molecular structure, are generally obtained. Although the theoretical treatment of ^{19}F chemical shifts and coupling constants is not well developed, empirical correlations are very useful (chapter 4). In this study of some fluorine compounds of tungsten, considerable dependence has been put on ^{19}F n.m.r. spectroscopy for the characterisation of reaction products. The identification of tungsten-fluorine compounds is generally straightforward, as the resonances of fluorine atoms directly bonded to tungsten have satellite peaks arising from spin-spin coupling with the tungsten-183 isotope ($I = \frac{1}{2}$, natural abundance ca. 14%).

Among the many known binary fluorides the hexafluorides form an interesting and, in some respects, an unusual class of compounds.

Hexafluorides are known for the group VI elements sulphur, selenium, tellurium and polonium, the rare gas xenon, chromium, and some of the second- and third-row transition and actinide metals. The physical and chemical properties of these highly symmetrical molecules have been extensively reviewed.[5, 6, 7, 8] Much of this material has appeared since the commencement of the work described in this thesis (October 1966) and provides some perspective for the present study of some of the chemical properties of tungsten hexafluoride.

The hexafluorides display a complete range of chemical behaviour, from inertness to remarkable reactivity. In general, the non-metal hexafluorides are less reactive than the metal hexafluorides, which show varying degrees of reactivity. Within the group of the second- and third-row metal hexafluorides, systematic variations in physical properties can be correlated satisfactorily with differences in chemical reactivity.

The most distinctive physical properties of the hexafluorides, and particularly of the metal hexafluorides, are their high volatilities and extremely short liquid ranges. High volatility is unexpected in view of the high molecular weights involved, and this is thought to arise from the absence of strong intermolecular forces between electronegative fluorine atoms. An unusual feature is that the hexafluorides of the third transition series are more volatile

than the corresponding hexafluorides of the second transition series. This phenomenon is inexplicable in terms of the conventional concept of an inverse relationship between molecular weight and volatility, and it has been suggested that, since the intermolecular forces are almost identical on the periphery of the molecules, entropy considerations are important.[9] Of the transition metal hexafluorides, tungsten hexafluoride, a colourless liquid, m.pt. 2.0°, b.pt. 17.1° (ref. 10), is the most volatile, and this property allows it to be handled by conventional vacuum-line techniques.

The infrared and Raman spectra of the hexafluorides of the second and third transition series have been interpreted on the basis of octahedral symmetry, and in some cases there is evidence of Jahn-Teller distortion.[11] Electron diffraction experiments also indicate octahedral symmetry and approximately constant metal-fluorine bond lengths (1.83 Å) in the third-row series.[12, 13] Force constants derived from vibrational spectra provide a convenient measure of the strength of chemical bonds, and a recent calculation of the stretching force constants for the metal-fluorine bonds of transition metal hexafluorides in the gaseous state gives the highest value for WF_6,[14] suggesting that it should be the most stable and therefore the least reactive chemically. The same conclusion might be drawn from the observation that the totally symmetric, a_{1g} mode, which is closest to a measure of the bond strength, has the highest

value for WF_6 and decreases along the series.[5] The frequencies of the a_{1g} modes for the third-row hexafluorides are higher than for the corresponding members of the second-row. The enthalpies of formation of molybdenum and tungsten hexafluorides have been determined by fluorine bomb calorimetry,[15, 16] and average bond energies of 107 and 121 kcal/mole respectively can be derived.[6] These values are much higher than those of sulphur, selenium and tellurium hexafluorides, which are 79, 73, and 81 kcal/mole respectively.[6, 17]

The available comparative studies of the chemical reactivities of the transition metal hexafluorides confirm the above predictions. Tungsten hexafluoride is the least reactive, and has been used as a solvent for n.m.r. studies of other fluorides.[18] Platinum hexafluoride, on the other hand, is extremely reactive. It can oxidise molecular oxygen[19] and xenon,[20] and can fluorinate bromine trifluoride to bromine pentafluoride.[21] From a study of the oxidative reactions of the hexafluorides of the third transition series with nitric oxide and nitrosyl fluoride, Bartlett and co-workers[6, 22] concluded that the electron affinities are in the order $WF_6 < ReF_6 < OsF_6 < IrF_6 < PtF_6$. They observed, however, that the ability of the hexafluorides to accept fluoride ion to give MF_7^- and MF_8^{2-} species decreases along this series, and they attributed the effect to a sharp increase in ligand crowding from WF_6 to PtF_6.

In order to account for the trends in the stability and reactivity of the metal hexafluorides, it has been suggested that there is fluorine-to-metal π-bonding, and that the contribution of π-bonding to the total bonding decreases as the number of electrons in the metal t_{2g} orbitals increases, resulting in decreasing stability and consequently increasing reactivity from left to right across the series.[5, 6] It is expected that π-bonding will be greater in the hexafluorides of the third transition series than in those of the second transition series because of the greater nuclear charges of the central atoms of the former. Bartlett[6] has suggested that the constancy of the M-F bond lengths in the third row hexafluorides[12, 13] may result from a coincidental matching of the lengthening from loss of multiple-bond character with the shortening from the transition series contraction.

Tungsten hexafluoride was prepared by Ruff and co-workers in 1905 by means of the reaction,

$$WCl_6 + 6HF \longrightarrow 6HCl + WF_6 \ (-2^{\circ} \text{ to } 20^{\circ}, \text{ in platinum}) \ ,$$

and they made the first qualitative investigations of its chemical behaviour.[23, 24] The direct action of fluorine on powdered tungsten is now preferred for the preparation of WF_6.[25, 26] Although the preparation, purification and physical characterisation of WF_6 is well documented, there have been, in common with the other metal hexafluorides, few investigations of its chemistry.

Molybdenum and tungsten hexafluorides were long regarded as very reactive compounds, and very similar in physical and chemical properties.[27] The assumption that their chemical properties are very similar appears to have been based on the similarity of their hydrolysis reactions. More recent work, however, indicates that there are considerable differences in chemical reactivity. O'Donnell and Stewart[28] have studied oxidation-reduction and halogen-exchange reactions of the higher fluorides of chromium, molybdenum and tungsten with lower fluorides of some non-metals and some non-metal chlorides, and have found that the order of reactivity is $CrF_5 > MoF_6 > WF_6$. MoF_6 is a weak fluorinating agent towards PF_3, CS_2 and WF_4, yielding PF_5, $(CF_3)_2S_2$ and WF_6 respectively, the other product in each case being MoF_5. Halogen-exchange occurs between MoF_6 and PCl_3, $AsCl_3$, $SbCl_3$, $TiCl_4$, CCl_4, $SiCl_4$, BCl_3 and PBr_3. WF_6 is virtually inert as a fluorinating agent, only reacting slowly with PF_3:

$$WF_6 + PF_3 \longrightarrow WF_4 + PF_5 \quad .$$

WF_6 undergoes halogen-exchange reactions with $TiCl_4$ and BCl_3 to yield WCl_6 and WCl_3F_3 respectively. A slow reaction also occurs between WF_6 and PBr_3 yielding WBr_5 and PF_3. The reactions of the hexafluorides of molybdenum, tungsten and uranium with binary ionic chlorides have been studied by O'Donnell and Wilson[29], and these provide further evidence of the relatively inert nature of WF_6

compared with MoF_6 and UF_6. Halogen exchange was observed between WF_6 and $BeCl_2$ to yield WCl_6 and BeF_2.

Tungsten hexafluoride forms intensely coloured solutions in organic donor solvents, indicating that weak molecular complexes are formed,[30, 31, 32] and isolable adducts are obtained with amines, amides and phosphines.[31, 33, 34, 35] The adduct $WF_6, 4.5SO_3$ is formulated as the fluorosulphate $WF_2(SO_3F)_4$ from which excess sulphur trioxide has not been removed, but the compound is not well characterised.[33] Reaction of WF_6 with benzene at 110° (7 days) yields tungsten tetrafluoride, WF_4,[36] and a recent report describes the cleavage of Si-O bonds in hexamethyldisiloxane and alkylalkoxysilanes by WF_6, but no tungsten-containing products were identified.[37]

Substituted derivatives of WF_6 are limited to the recently reported chlorofluorides $WF_{6-n}Cl_n$, n = 1-5, which are prepared either by exchange reactions with $TiCl_4$[38, 39] or BCl_3,[28] or by the controlled fluorination of WCl_6.[38, 39, 40] The ^{19}F n.m.r. spectrum of liquid WF_5Cl is consistent with the C_{4v} symmetry expected for a monomer, and both the vibrational[41] and microwave[41a] spectra are in accord with this conclusion. A number of complex fluorotungstates derived from WF_6 containing the anions WF_6^-, WF_6^{2-}, WF_7^- and WF_8^{2-} have been described.[6, 42-45, 83, 84]

The earlier literature on other tungsten fluorides and

oxofluorides has been recently reviewed.[5] Tungsten pentafluoride has recently been prepared by reaction of WF_6 with a tungsten wire at 500-700°,[46] and has been shown, from crystallographic powder data,[47] to be isomorphous with molybdenum, niobium and tantalum pentafluorides which have a tetrameric unit in the solid state, the four metal atoms being linked by approximately linear bridging fluorine atoms, and each metal atom having a distorted octahedral coordination completed by four terminal fluorine atoms.[3, 4] The only other known fluoride of tungsten is the tetrafluoride, WF_4, which has been obtained from the reaction of WF_6 with PF_3,[28] from the reaction of WF_6 with benzene,[36] and from the disproportionation of WF_5 at 50°-70°.[46] Tungsten tetrafluoride is not well characterised.

Several oxofluorides of tungsten have been described. The best known is the oxotetrafluoride, WOF_4, but there is some controversy about the structure of this compound. Blanchard[48] has interpreted the infrared spectrum of gaseous WOF_4 in terms of a monomeric unit with C_{4v} symmetry, and has assigned a band at 1055 cm^{-1} to a W=O stretching mode. Ward and Stafford[49] have also published vapour phase infrared spectral data for WOF_4, but their values are significantly different from those of Blanchard. Edwards and co-workers[50] have interpreted the data from a crystal structure analysis of WOF_4 in terms of a tetrameric molecular unit with tungsten atoms at the corners of a square, linked by nearly linear bridging oxygen

atoms. Fluorine atoms complete the slightly distorted octahedral coordination about each tungsten atom. This structure is similar to those of niobium,[3] tantalum[3] and molybdenum[4] pentafluorides, but is different from that of molybdenum oxotetrafluoride, which has an infinite chain arrangement with cis-bridging fluorine atoms and terminal oxygen atoms.[51] Edwards and coworkers[50] have interpreted the infrared spectrum of WOF_4 in the solid state on the basis of their crystal structure analysis, and assign a prominent absorption at 1050 cm^{-1} (in the region normally associated with metal-oxygen double-bond stretching frequencies[52]) to a W-F stretching frequency associated with a short bond of 1.65 Å, and part of the band system at 650 cm^{-1} to the stretching vibrations of the W-O-W bond system.

Beattie and Reynolds[53] have examined the Raman spectrum of WOF_4 in the solid state and in the melt, and they disagree with the conclusions of Edwards and co-workers. They assign an intense band at 1058 cm^{-1} in both the solid state and the melt to a terminal W=O stretching mode, and bands in the region of 700 cm^{-1} to terminal fluorine stretching modes. They point out that the assignment of the atomic positions of light atoms in a crystal structure determination in cases where there is one very heavy atom (W) and two closely similar light atoms (O, F) is, at best, tenuous, and suggest that the correct placing of the tungsten atoms with oxygen or fluorine atoms in any of the "correct" light atom positions would provide a "solution"

of the structure. They conclude that WOF_4 is a fluorine-bridged polymer in the solid state and in the melt. Tebbe and Muetterties[35] have observed a single line ^{19}F n.m.r. resonance for WOF_4 in sulphur dioxide solution, and have prepared and characterised salts containing the WOF_5^- ion.

Tungsten dioxodifluoride, WO_2F_2, has been reported as a hydrolysis product of WF_6[54] and WOF_4,[24] and recently, mass spectroscopic evidence for its existence in the vapour phase has been published.[55] The chemistry of WO_2F_2 is, however, unexplored. Tungsten oxodifluoride, WOF_2, has been described as a stable, grey, graphite-like powder obtained from the reaction of tungsten dioxide with HF at 300-800°,[36] but recent Russian work casts considerable doubt on the existence of the compound.[56]

Binary fluorides have been widely used as fluorinating agents, particularly in organic chemistry (e.g. sulphur tetrafluoride[57]), and tungsten hexafluoride has been described both as a powerful fluorinating agent[27] and as having no fluorinating action.[58] Both of these conclusions are based on few experimental observations. The more recent experimental work outlined above leads to the conclusion that WF_6 is the least reactive of the transition metal hexafluorides, and is less easily reduced than MoF_6 or UF_6. The present work was undertaken with a view to extending the extremely limited chemistry of WF_6. The reactions of WF_6 with benzene at

elevated temperatures,[36] with acetone[31] and diethyl ether[32] at ambient temperatures, although incompletely described, suggested that WF_6 might act as a mild, selective fluorinating agent. A further aim of this study was the preparation of derivatives of WF_6, and an investigation of their physical and chemical properties.

CHAPTER ONE

SOME MOLECULAR COMPLEXES OF TUNGSTEN HEXAFLUORIDE AND ITS REACTIONS WITH ETHERS, THIOETHERS AND SELENOETHERS

Introduction

There is no rigorous definition of the term "molecular (or addition) complex", and it is used both in inorganic and organic chemistry to describe the products of a wide variety of types of association between two or more molecules. It has been applied both to stable isolable complexes, such as those formed between binary halides and strong Lewis bases, and to a large class of complexes formed by the weak interaction of certain organic donor molecules with a wide variety of Lewis acids, which, although their compositions can be represented by integral mole ratios of components, are generally so unstable that they exist only in solution or in the gas phase in equilibrium with their components. The formation of this latter type of complex is generally attended by the development of very intense colours. Molecular complexes are to be distinguished, however, from clathrate or occlusion compounds, in which there is no interaction between the two components. As the nature of the intermolecular forces in

molecular complexes is still the subject of considerable controversy, it is convenient to use the label "donor-acceptor complex", and thus circumvent the difficulty of specifying the nature of the bonding involved. Molecular complexes and methods of studying them have been extensively reviewed.[59, 60, 61]

A prerequisite of the formation of a donor-acceptor complex between two molecules whose valencies are already satisfied is the presence of energetically suitable orbitals in both the donor and the acceptor. A bond is formed when there is electron transfer from a filled orbital of the donor to a vacant orbital of the acceptor. Mulliken has classified donor-acceptor complexes on the basis of the types of orbitals used in bond formation.[62] Donor molecules are considered as n, σ, or π according to whether the electrons available for donation are non-bonded electrons (i.e. lone pairs), electrons in σ-bonds, or electrons in π-molecular orbitals respectively. Acceptor molecules are similarly classified as v, σ or π according to whether the electrons are accepted into vacant valency orbitals, non-bonding σ-orbitals, or a system of π-bonds respectively. In principle any donor can combine with any acceptor, and the complexes are denoted by the combination of the appropriate symbols.

WF_6 has vacant 5d-orbitals, and is a v-acceptor. Complexes of WF_6 with a variety of n- and π-donors have been reported.[30-35] Priest and Schumb were able to make an approximate correlation of the colours

of solutions of WF_6 in various organic n- and π-donor solvents with the presence of certain functional groups.[30] Solutions of WF_6 in benzene and of WF_6 and benzene in carbon tetrachloride were found to obey Beer's Law, and the formation of a 1:1 $WF_6.C_6H_6$ complex is postulated. Winfield has examined the ^1H and ^{19}F n.m.r. spectra of solutions of WF_6 in benzene, toluene, hexafluorobenzene and carbon tetrachloride, but did not find any correlation between the donating power of the organic molecule and the chemical shift of the ^{19}F nuclei in WF_6, small shifts in the positions of the resonances being attributed to solvent effects.[32] A slow reaction occurs between WF_6 and diethyl ether with the deposition of a brown solid, and the ^{19}F n.m.r. spectrum of a freshly prepared solution of WF_6 in diethyl ether shows a broadened featureless signal of low intensity, 1 p.p.m. upfield from pure WF_6. This is accounted for in terms of either the presence of a paramagnetic species from reduction of WF_6, or an equilibrium between uncomplexed and complexed WF_6:

$$WF_6 + xEt_2O \rightleftharpoons WF_6.(OEt_2)_x \quad .$$

WF_6, like PF_5[63] polymerises tetrahydrofuran.

The visible spectra of solutions of WF_6 in benzene, hexafluorobenzene and pentafluorobromobenzene have been recorded by Mercer.[31] The value of λ(wavelength) for the absorption associated with the formation of the complex increases with increasing electron-donating power of the donor.

In his original study of the complexes of WF_6 with amines, amides and phosphines, Muetterties postulated the structure $[WF_5.base]^+ F^-$ for the complexes on the basis of their ^{19}F n.m.r. spectra which consisted of a doublet, a quintet and a singlet in the required intensity ratio.[34] However a further report by Tebbe and Muetterties on the nature of adducts of WF_6 shows that the original structural characterisation of these complexes is in error because of hydrolysis.[35] The complex $WF_6.PMe_3$ in sulphur dioxide solution decomposes by reaction either with the solvent or with trace amounts of water to give the WOF_5^- ion as one of the products, and the spectral parameters originally assigned to $[WF_5.base]^+ F^-$ structures are identical with those of the WOF_5^- ion in authentic samples (see below under "Hydrolysis Products of Tungsten Hexafluoride Derivatives"). The singlet originally assigned to the fluoride ion is not reproducible in the ^{19}F n.m.r. spectra of WF_6 complexes.

The ^{19}F n.m.r. spectrum of $WF_6.PMe_3$ provides a fairly rigorous demonstration of seven-coordination for tungsten.[35] The spectrum in sulphur dioxide and acetonitrile consists of a doublet arising from $^{31}P-^{19}F$ coupling, with satellite doublets from $^{183}W-^{19}F$ coupling. The signal is unperturbed down to -85°. It is suggested that since strict equivalence of fluorine atoms in any of the idealised seven-coordinate geometries is not possible, spectroscopic equivalence results from a rapid intramolecular rearrangement through which

fluorine atom environments are averaged. N.m.r. spectroscopic equivalence of ligand atoms has been observed for the seven-coordinate molecules IF_7 and ReF_7.[64]

The complexes of WF_6 with nitrogen bases[35] also show spectroscopic equivalence of fluorine atoms, but in this case the possibility of equivalence arising from the fast dissociation process,

$$WF_6 \cdot NR_3 \rightleftharpoons WF_6 + NR_3$$

cannot be eliminated, as there is no observable spin-spin coupling between the fluorine and the nitrogen nuclei. Both the 1:1 and 1:2 adducts of WF_6 with pyridine show single-line ^{19}F n.m.r. resonances, that of the 1:2 adduct being at higher field to that of the 1:1 adduct. The resonance of the 1:2 adduct moves to higher field as the temperature is lowered consistent with the equilibrium:

$$WF_6 \cdot py_2 \overset{\Delta}{\rightleftharpoons} WF_6 \cdot py + py$$

Several workers have observed the cleavage of dialkyl ethers by transition metal halides. Fowles and Frost have obtained $WOCl_3, 2C_4H_8O$ from the reaction of tungsten hexachloride with tetrahydrofuran, a process which evidently involves both reduction of the tungsten and oxygen abstraction from excess ligand.[65] Complexes of molybdenum oxotrichloride, $MoOCl_3$, have been prepared by reaction of molybdenum pentachloride with a variety of ethers.[66, 67] The reaction of $MoCl_5$

with dioxane yields 2,2'dichloroethyl ether in addition to a $MoOCl_3$ complex.[67]

The pentahalides of niobium and tantalum form stable adducts with ethers and thioethers. The pentafluorides form stable 1:1 adducts with dimethyl and diethyl ethers and thioethers, all of which can be distilled unchanged at low pressures with only slight dissociation into the pentafluoride and ligand. The pentafluorides form 1:2 adducts with tetrahydrothiophen, dimethyl ether and dimethyl sulphide, though in the latter two cases the adducts are stable only at low temperatures.[68] The pentachlorides form stable 1:1 complexes with dimethyl,[69] diethyl,[70] and di-n-propyl[69] ethers, and 1,4 dioxane;[71,72] smaller-ringed cyclic ethers such as tetrahydrofuran and propylene oxide are broken and polymerise.[72] The diethyl ether and di-n-propyl ether adducts of the pentachlorides decompose below 100° to give the metal oxotrichlorides and alkyl chlorides.[70] Stable 1:1 complexes are also formed between the pentachlorides and dimethyl sulphide, diethyl sulphide[73] and di-n-propyl sulphide,[69] and there is some evidence for the formation of $TaCl_5,2Me_2S$.

The complexes of niobium and tantalum pentachlorides with diethyl sulphide are thermally more stable than those formed with diethyl ether, and diethyl ether is readily displaced from a complex by diethyl sulphide. Dimethyl ether, however, is not displaced by dimethyl sulphide from its complexes with niobium(V) and tantalum(V) chlorides, nor is Me_2S displaced by Me_2O from the complex $TaCl_5,Me_2S$. The

greater strength of the metal-sulphur as compared with the metal-oxygen bond in the case of the Et_2S and Et_2O complexes of the pentachlorides has been attributed to the greater polarisability of the sulphur atom, and the greater dipole moment of the sulphur-containing ligand.[69] A similar example of the same effect has been found in the thioxane complexes, MCl_5, C_4H_8OS, (M = Nb, Ta), where infrared and n.m.r. spectral data indicate that the ligand coordinates via sulphur and not oxygen.[71]

Niobium and tantalum pentabromides form stable 1:1 complexes with diethyl ether and with 1,4 dioxane,[70] and molecular weights for the latter are close to the values expected for monomeric species.[71] The diethyl ether adducts of the pentabromides decompose on warming to yield ethyl bromide and the corresponding metal oxotribromide. Stable 1:1 complexes are also formed between the pentabromides and dimethyl and diethyl sulphides,[73] and the bonding in the thioxane complexes is via the sulphur atom.[71]

The work described in this chapter was undertaken with a number of objectives. Firstly, a Raman spectroscopic examination of solutions of WF_6 in organic donor solvents was undertaken with a view to obtaining information about the nature of the species in solution. Infrared and Raman spectroscopy have been widely used in the study of molecular complexes.[59] Complex formation is usually accompanied by significant shifts in the positions of absorptions characteristic of

the donor and the acceptor, and the appearance of new absorptions as a result of the lowering of the total symmetry of the system. For example, it has recently been shown by Klaboe that the Raman frequencies of iodine, bromine and iodine monochloride in n- and π- organic donor solvents are at considerably lower energy than the corresponding gas values.[74] The formation of a 1:1 complex between WF_6 and benzene[30] should result in some distortion of the O_h symmetry of WF_6. Although this distortion is not observed by ^{19}F n.m.r. spectroscopy,[32] it was thought that it might be detectable by vibrational spectroscopic techniques which have a considerably shorter time scale (10^{-13} sec.) than n.m.r. (10^{-1} - 10^{-9} sec.).[75] Raman spectroscopy was chosen in preference to infrared spectroscopy as all-glass equipment can be used, thus rendering the technique less difficult experimentally for these extremely hygroscopic solutions.

Secondly, the preparation of a solid complex of WF_6 with a polycyclic aromatic hydrocarbon was attempted. Such a complex would be useful for further physical studies of the nature of the interaction. 1-methylnaphthalene and 9-methylanthracene were chosen as donors, the former because it is a liquid at ambient temperatures, the latter because of its high solubility in suitable solvents.

Thirdly, the high solubility of WF_6 in organic donor solvents suggested that they might provide useful media for the preparation of hexafluoride complexes and their spectroscopic study in solution.

Complex fluorotungstates were chosen for study, and nitromethane was selected as a suitable solvent. Previous workers have used iodine pentafluoride, arsenic trifluoride and sulphur dioxide as reaction media for the preparation of fluorotungstates.[43] This section of the work is largely of a preliminary nature.

Fourthly, it was felt that further examination of the reduction of WF_6 to WF_4 by benzene at elevated temperatures[30] was necessary. It was hoped to identify the organic products of this reaction, and some investigation of the physical and chemical properties of WF_4 seemed desirable.

Fifthly, as previous investigations[30, 32] had indicated that a slow reaction occurs between WF_6 and dialkyl ethers, the reactions of WF_6 with dimethyl and diethyl ethers under forcing conditions were examined. This work was extended to include reactions of WF_6 with thioethers, selenoethers and dimethyl disulphide. It was of some interest to compare the behaviour of WF_6 towards these reagents with that of other similar transition metal halides.

Preliminary accounts of some of the work described in this chapter have been published.[76, 77]

The Nature of Tungsten Hexafluoride in Solution

An octahedral molecules has six normal modes of vibration, of which two, ν_3 and ν_4, are infrared active, and three, ν_1, ν_2 and ν_5, are Raman active.[11] The Raman spectra of WF_6 in benzene (π-donor), acetonitrile (n-donor), and cyclopentane are summarised in Table 1.1.

TABLE 1.1

Raman spectra of WF_6 in various solvents

Solvent	Solution Colour	Vibrational frequencies (cm^{-1})[a] ν_1	ν_2	ν_3	ν_4	ν_5	Ref.
WF_6	colourless	769	670	-	-	322	78
		772	672	-	-	316	79
C_6H_6	red	770 (vs.p)	670 (w.dp)	-	261 (vw.dp)	326 (m.dp)	
CH_3CN	yellow	773 (vs)	677 (w)	707 (vw)	269 (vw)	328 (m)	
cyclo C_5H_{10}	colourless	772 (vs)	676 (w)	-	266 (vw)	326 (m)	
WF_6, gas phase		771	671	711	258	319	80

[a] Values for the present work are ± 2 cm^{-1}

No donor-acceptor interaction is expected in cyclopentane, and it can be seen that, within experimental error, there are no significant shifts of the Raman active vibrations of WF_6 in the coloured solutions. The Raman forbidden vibrations ν_3 and ν_4 are weakly observed in acetonitrile, and ν_4 in benzene. However ν_4 is also weakly observed in cyclopentane, and is clearly visible in the published spectrum of WF_6 by Burke and co-workers.[79] These forbidden bands could arise from weak intermolecular interactions in the liquid phase.

The experiments indicate that the extent of donor-acceptor interaction in these intensely coloured solutions in small, and that the octahedral symmetry of WF_6 is maintained. Hammond and Lake have recently stated that the colours of solutions of the highest valency halides, including WF_6, in aromatic hydrocarbons and fluorocarbons disappear on freezing, and conclude that all donor-acceptor interactions are very weak and have near zero equilibrium constants.[81] Studies of the u.v. and visible spectra of weak molecular complexes of WF_6 in the gas phase, carried out in these laboratories by McLean,[82] have led to the same conclusion.

The coloured solutions of WF_6 in n- and π-donor solvents provide examples of systems where there are "charge transfer" interactions. It is envisaged[62a] that a photon is absorbed by the weak complex between the electron donor (D) and the electron acceptor (A), with

the consequent transfer of an electron from the donor to the acceptor. The complex is considered to be stabilised by the small interaction of a no-bond ground state (D, A) with a polar excited state ($D^+ A^-$), to give two electronic states which can be approximately described by the wavefunctions:

$$\text{Ground state,} \qquad \Psi_N = \Psi(D, A) + \lambda\Psi(D^+ A^-)$$

$$\text{Excited state,} \qquad \Psi_E = \Psi(D^+ A^-) - \mu\Psi(D, A)$$

where λ and μ are small compared with unity. The absorption spectrum is then associated with the electronic transition $\Psi_N \rightarrow \Psi_E$.

The Interaction of Tungsten Hexafluoride with Aromatic Hydrocarbons

A solution of WF_6 in 1-methylnaphthalene is dark red, and a solution of WF_6 and 9-methylanthracene in carbon tetrachloride is dark green. In both cases coloured solids are formed, but these have not been characterised. The dark green solid formed from the interaction of WF_6 with 9-methylanthracene in CCl_4 does not give consistent elemental analyses, and has a very low fluorine content. No definite conclusions can be drawn about the nature of these products.

Several attempts were made to repeat the reduction of WF_6 with benzene at 110°,[36] but no reaction was observed. This reaction may be sensitive to the amounts of reactants used, or may have been catalysed originally by trace amounts of moisture.

The Preparation of Tetraalkyl Ammonium Hexafluorotungstates

Tungsten hexafluoride dissolves readily in nitromethane to yield a pale yellow solution, and reasonably pure samples of the tetraalkyl ammonium hexafluorotungstates $R_4N^+WF_6^-$, R = ^nBu, ^nPr, are obtained by reaction of WF_6 with the appropriate tetraalkyl ammonium iodide in nitromethane according to the equation:

$$R_4NI + WF_6 = R_4NWF_6 + \tfrac{1}{2}I_2 \quad . \qquad (1.1)$$

The compounds are characterised by elemental analyses, infrared spectroscopy, and conductivity measurements. There are significant splittings of both of the i.r. active vibrations of the WF_6^- ion in these compounds (Table 1.2), and these splittings are thought to arise from the effect of the large cation on the lattice structure. The equivalent

TABLE 1.2

Infrared spectra of some hexafluorotungstates

Compound	Infrared active vibrations (cm^{-1}) ν_3	ν_4	Ref.
$^nBu_4NWF_6$	650, 615	248[a]	
$^nPr_4NWF_6$	625, 605	250, 236	
$CsWF_6$	590	249, 230	83
KWF_6	594	249, 230	83

[a] Lower absorption not observed in this case.

conductivity of $^{n}Bu_4NWF_6$ in nitromethane (Λ = 90-100 ohm^{-1} cm^{2}) is in the range found for 1:1 electrolytes in this solvent,[85] but the value in acetonitrile is low for a 1:1 electrolyte. The ultraviolet spectra of solutions of $^{n}Bu_4NWF_6$ and $^{n}Pr_4NWF_6$ in CH_3CN showed absorptions at 31,750 and 32,470 cm^{-1} respectively, with extinction coefficients (ϵ = 100-130) of the order expected for d-d transitions. These values agree well with the published value for the d-d transition of the WF_6^- ion (32,400 cm^{-1}) obtained from ultraviolet reflectance spectra.[84] The present work indicates that the WF_6^- ion is stable in acetonitrile and nitromethane solution.

The Reactions of Tungsten Hexafluoride with Ethers. Preparation and Properties of Oxotetrafluoro(dimethyl ether)tungsten(VI)

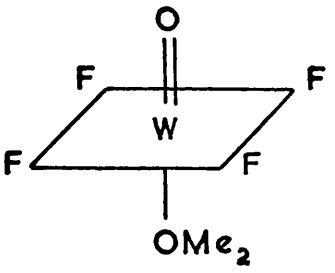
The reactions of WF_6 with dimethyl and diethyl ethers are complex, and the products depend on the conditions used. The major product of the prolonged reaction of WF_6 with excess dimethyl ether in a stainless-steel vessel at 110° is a colourless, volatile liquid, m.p. ca. 10°, formulated as oxotetrafluoro(dimethyl ether)tungsten(VI), $WOF_4.OMe_2$, on the basis of analytical and spectral data. Reaction of WF_6 with excess diethyl ether under similar conditions yields a colourless, volatile liquid, thought to be $WOF_4.OEt_2$ as its infrared spectrum and properties are similar to those of $WOF_4.OMe_2$. However $WOF_4.OEt_2$ is not well characterised, as it decomposes readily during the reaction work-up. The other volatile products of the reaction of

WF_6 with Me_2O are small quantities of methyl fluoride and SiF_4. The latter indicates the formation of a small quantity of HF, either as a reaction product or as a product of some hydrolysis during the work-up. Under all conditions used, some reduction of WF_6 occurs to yield black, lustrous solids of variable composition (W:F = 4.6:1 - 1:4.4), which contain some carbon and hydrogen. These have not been identified, but peaks in their infrared spectra in the regions 3060-2850, 1025-920, and 710-600 cm^{-1} are not inconsistent with a mixture of lower tungsten oxofluorides and organic material. The reaction of WF_6 with dimethyl ether is therefore consistent with:

$$WF_6 + \text{excess } Me_2O \xrightarrow[65\text{hrs}]{110^{\circ}} WOF_4.OMe_2 + MeF + HF(?) + \text{lower oxofluorides + polymers} \quad (1.2)$$

The yield of $WOF_4.OMe_2$ in 1.2 is 60%, but is sensitive to reaction time and conditions.

The mass spectrum of the liquid product formulated as $WOF_4.OMe_2$ consists of peaks arising from WF_4O^+, $C_2H_6O^+$ and their fragments, but does not show a parent ion, consistent with the lability of Me_2O in the complex. The ^1H and ^{19}F n.m.r. spectra (Table 1.3) both consist of a single peak, the ^{19}F signal having satellite peaks from ^{183}W - ^{19}F coupling. The ^{19}F n.m.r. spectrum is consistent with a monomeric, octahedral structure (I) in which the ether ligand occupies a position



(I)

trans to the terminal W=O bond, but it is not definitive, as a single line resonance with ^{183}W - ^{19}F satellite peaks could also result from rapid rearrangement of a polymeric structure in which no tungsten-fluorine bonds are broken. The ^{19}F chemical shift and ^{183}W - ^{19}F coupling constant are similar to those reported for WOF_4 in SO_2, and for the equatorial fluorine atoms in the WOF_5^- anion.[35]

TABLE 1.3

N.m.r. spectra of tungsten(VI) oxofluoride complexes

Compound	Solvent	Spectrum Type	δ_F, p.p.m. (rel.CCl_3F)	δ_H τ	J_{WF} Hz	J_{FF} Hz	Ref.
$WOF_4.OMe_2$	neat	single line	-62.8	6.31	68		
$W_2O_2F_9^-$ in $WOF_4.OMe_2$		AX_8	-60.3 (F_X) +146.0 (F_A)		71 51	58	
WOF_4	SO_2	single line	-73.9		64		35
$^nPr_4N^+WOF_5^-$	CH_3CN	AX_4	-49.4 (F_X) +82.8 (F_A)		70	53	35
$^nPr_4N^+WOF_5^-$	SO_2	AX_4	-54.3 (F_X) +71.9 (F_A)		71	52	35

The ambiguity which exists in the assignment of infrared absorptions to W=O (terminal), W-O-W, W-F (terminal) and W-F-W stretching modes in relatively simple molecules[50, 55] prevents a definite assignment of the infrared spectrum of $WOF_4.OMe_2$. However the assignments in Table 1.4 are consistent with the structure (I). Terminal metal-oxygen groups generally give rise to a strong band ca. 1000 cm^{-1},[52] and the assignment of a strong band

TABLE 1.4

Infrared Spectrum of $WOF_4.OMe_2$

$WOF_4.OMe_2$ cm^{-1}	Assignments	Me_2O (in C_6H_6)[86] cm^{-1}
1255, 1156	$\delta(CH_3)$	1470, 1456, 1164
1045	ν(COC) asymm	1093
1025	ν(W=O)	
883	ν(COC) symm	918
853, 815	ν(WOC) (?)	
700, 667, 640	ν(WF)	
456	δ(COC)	424

at 1025 cm^{-1} to a W=O stretching mode is consistent with this. A prominent shoulder at 1045 cm^{-1} is assigned to the C-O (asymm) stretch of coordinated Me_2O. The antisymmetric and symmetric ether C-O stretching modes show characteristic shifts to lower energy of 48 and

35 cm^{-1} respectively on coordination. The assignment of the bands in the region 853-640 cm^{-1} is less convincing, as the absorptions of a W-O-W group would occur in this region.[52a] Assignments similar to those in Table 1.4 have been made for the infrared spectra of ether complexes of BF_3,[87] $AlCl_3$,[86, 88] and tungsten oxohalides.[65, 66]

The spectra and volatility of $WOF_4.OMe_2$ suggest that it is monomeric, though a polymeric structure cannot be excluded completely. A similar compound, $WOCl_4.MeCN$, is monomeric in benzene solution.[65] $WOF_4.OMe_2$ dissociates to a small extent at 20°, and decomposes rapidly in the presence of trace amounts of moisture or impurities, depositing white solids. It reacts vigorously with sodium fluoride and tetraethylammonium chloride with evolution of Me_2O, to yield white and yellow solids respectively. These products have not been characterised, but contain tungsten and fluorine. It is possible that ligand replacement reactions occur:

$$WOF_4.OMe_2 + X^- \longrightarrow WOF_4X^- + Me_2O \quad , \quad X = F, Cl \qquad (1.3)$$

Compounds containing the WOF_5^- anion have been described,[35, 89] but WOF_4Cl^- is unknown. These reactions provide scope for future work.

Although complexes of $WOCl_4$ and $WOBr_4$ with ethers, alkyl cyanides and pyridine have been described,[65] the only adducts of WOF_4 which have been reported are $WOF_4,0.5NH_3$,[24] $WOF_4.IF_5$, $WOF_4.SeOF_2$ and $WOF_4.SeF_4$.[89] However, the formulation of these compounds as adducts of WOF_4 is based only on analytical data, and no spectroscopic

properties are described.

Pentafluoromethoxotungsten(VI), WF_5OMe, has been prepared in this work (chapter 2), and it decomposes, slowly at ambient temperatures and rapidly above 100°, to yield WOF_4 and methyl fluoride. It also reacts with dialkyl ethers to yield products similar to those obtained from the reactions of WF_6 with dialkyl ethers. The following processes involving the initial formation of a donor-acceptor complex, can thus be visualised for the reactions of WF_6 with Me_2O:

$$WF_6 + xMe_2O \longrightarrow WF_6.(OMe_2)_x \longrightarrow WF_5OMe + MeF + (x-1)Me_2O$$

$$WF_5OMe + Me_2O \longrightarrow WOF_4.OMe_2 + MeF \qquad (1.4)$$

Similar processes have been observed in the cleavage of dialkyl ethers with boron trihalides.[90]

The formation of a WOF_4 complex in the reaction of WF_6 with dimethyl ether demonstrates the great stability of a tungsten-oxygen multiple bond, and this reaction is the first example of oxygen abstraction from an ether by a transition metal fluoride.

The Reactions of Tungsten Hexafluoride with Thioethers and Selenoethers

WF_6 is readily miscible with dialkyl sulphides forming intensely brown (Me, Et) or purple (^iPr) solutions. A solution of WF_6 in dimethyl disulphide is also dark brown. WF_6 and diethyl sulphide react slowly at 20° to yield a yellow viscous liquid, formulated as hexafluorobis(diethyl sulphide)tungsten(VI), $WF_6(Et_2S)_2$, on the basis of full elemental analysis. This complex dissociates slightly at 20°

in vacuo, and can be distilled slowly at 50°. It decomposes at 100° to a black intractable tar, and does not dissolve in or react with diethyl ether. WF_6 and diethyl selenide react vigorously at 20° to yield an orange viscous liquid, formulated as hexafluoro-bis(diethyl selenide)tungsten(VI), $WF_6(Et_2Se)_2$, on the basis of elemental analysis. This complex dissociates slightly at 20°, and is involatile. Reactions of WF_6 with dimethyl sulphide and dimethyl selenide give ill-defined solids which decompose readily at ambient temperatures. Reaction of WF_6 with dimethyl disulphide yields a brown solid, for which elemental analysis suggests the formulation $(WF_6)_2(Me_2S_2)_3$. There is some evidence for the formation of a colourless liquid complex of WF_6 with diisopropyl sulphide, but its rate of formation at 20° is extremely slow, and it has not been characterised.

A monomeric, non-ionic formulation of the complexes $WF_6(Et_2S)_2$ and $WF_6(Et_2Se)_2$ requires coordination numbers of eight for tungsten, and it is expected that rapid intramolecular rearrangements will produce n.m.r. spectroscopic equivalence of fluorine atoms as observed for similar complexes of WF_6 with amines and phosphines.[35] The ^{19}F and ^{1}H n.m.r. data for these complexes are listed in Table 1.5. Considerable difficulty was experienced in obtaining ^{19}F n.m.r. signals for $WF_6(Et_2S)_2$ and $WF_6(Et_2Se)_2$, and the values in Table 1.5 were obtained for only one sample of each complex. These resonances were

TABLE 1.5

N.m.r. spectra of adducts of tungsten hexafluoride

Compound	Solvent	Temp.	δ_F, p.p.m. (rel. CCl_3F)	δ_H (CH_3) τ	δ_H(CH_2) τ	J_{WF} Hz	other J s Hz	Ref.
WF_6	neat	33°	-164.8			44		35,76
$WF_6 \cdot PMe_3$	SO_2	-20°	-137.4			38	73(PF)	35
$WF_6 \cdot NMe_3$	SO_2	28°	-144.8					35
$WF_6 \cdot NC_5H_5$	SO_2	28°	-163.9					35
$WF_6 \cdot (NC_5H_5)_2$	SO_2	25°	-135.9					35
$WF_6 \cdot (SEt_2)_2$	neat	33°	-70.8	8.5[a]	6.8[a]			
$WF_6 \cdot (SeEt_2)_2$	neat	33°	-143.7	8.5[a]	6.8[a]			
Et_2S	neat	33°		8.77	7.45			
Et_2Se	neat	33°		8.64	7.47			

[a] Mid-points of complex multiplets, externally referenced (± 0.1τ).

broadened single lines, and WF satellite peaks were not observed.

In other attempts ^{19}F n.m.r. signals could not be detected either for the neat liquids or for acetonitrile solutions, and the possibility of the reported resonances arising from hydrolysis products is not excluded.

The ^{1}H n.m.r. spectra of neat $WF_6(Et_2S)_2$ and $WF_6(Et_2Se)_2$ are reproducible, and the signals show small downfield shifts from the free ligands. The spectra do not show the expected triplet-quartet structure, but consist of two complex multiplets with intensities in the ratio 3:2. Examination of the spectra at two frequencies (60 and 100 MHz) does not yield evidence of chemically shifted ethyl groups, and it is thought that the complexity of the spectra arises from magnetic non-equivalence of the methylene protons in the ethyl groups,[91] rather than from non-equivalence of ligand sites. Magnetic non-equivalence of methylene protons in coordinated thioether and seleno-ether ligands arises from coordination in the direction of one of the lone pairs of the donor atom, and this effect has been invoked to explain the ^{1}H n.m.r. spectra of $Et_2S.BH_3$[92] and $[(PhCH_2)_2S]_2PtCl_2$.[93] The ^{1}H n.m.r. spectrum of $WF_6(Et_2Se)_2$ does not simplify to a triplet-quartet up to its decomposition point (100^{o}), suggesting that the rate of exchange between the two possible selenium coordination sites is slow at this temperature.

Hydrolysis Products of Tungsten Hexafluoride Derivatives. The $W_2O_2F_9^-$ ion

Since WF_6 and its derivatives hydrolyse extremely readily, great care must be taken to exclude trace amounts of moisture from all reaction systems. HF is a product of hydrolysis, and it attacks glass, initiating a hydrolytic cycle which can lead to complete loss of product:

e.g. $2WF_6 + 6H_2O = 2WO_3 + 12HF$

$12HF + 3SiO_2 = 3SiF_4 + 6H_2O$

In practice it is seldom possible to exclude moisture completely, particularly from n.m.r. tubes, which deform easily when subjected to high temperatures, and in some cases small amounts of tungsten-containing hydrolysis products are observed. The extent of hydrolysis in any reaction can be assessed from the amount of SiF_4 in the volatile fractions, and, provided that tungsten-fluorine reaction products are stored at low temperatures, hydrolysis is generally negligible. In some cases, however, HF is a reaction product (cf. WF_6 and dimethyl sulphoxide, chapter 2), and considerable hydrolysis occurs. It is desirable, therefore to characterise hydrolysis products to avoid confusion with reaction products.

The controlled hydrolysis of WF_6 in HF has been studied by conductivity and isothermal solubility methods,[54, 94] and the products are formulated as WO_2F_2 and $WO_2F_4^{2-}$. The equilibrium constant for the reaction,

$$WF_6 + 2H_2O \rightleftharpoons WO_2F_2 + 4HF$$

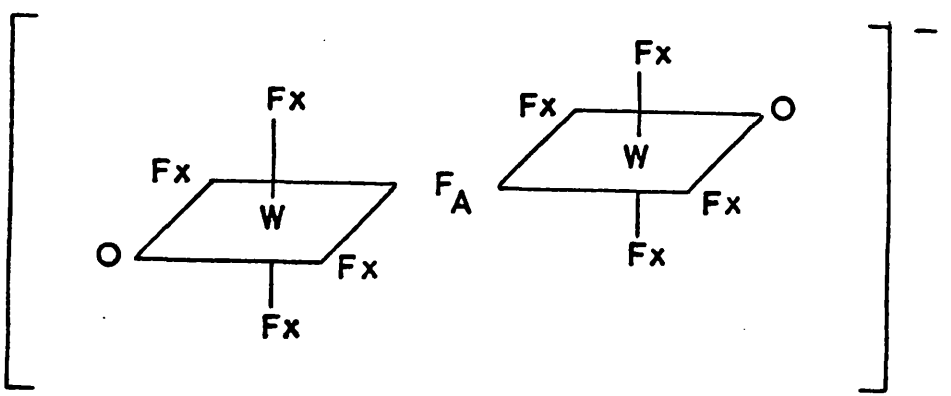
is given as 6×10^2.

Tebbe and Muetterties have shown that complexes of WF_6 decompose readily to yield the WOF_5^- ion.[35] The ^{19}F n.m.r. spectrum of a sample of $WF_6.PMe_3$ in sulphur dioxide solution indicates that an irreversible reaction occurs above -20°, either with the solvent or with trace amounts of moisture, to produce a sample with major peaks at -147.4 p.p.m. (rel. to CCl_3F, multiplicity of this signal is not given) and -64.3 p.p.m. (doublet, J = 63 Hz, J_{WF} = 74 Hz) and peaks of small intensity at +128.6 p.p.m. (multiplet, with a minimum of four lines, J = 12 Hz) and +145.4 p.p.m. (multiplet, with a minimum of five lines, J = 13 Hz), in addition to lines characteristic of WOF_5^- (Table 1.3). At room temperature, the intensity of the signals attributed to WOF_5^- increases as the intensity of the doublet at -64.3 p.p.m. diminishes. Decomposition of $WF_6.PMe_3$ does not occur as rapidly in acetonitrile as in sulphur dioxide.

Some of the ^{19}F n.m.r. spectra of the derivatives of WF_6 described in this chapter contain minor signals which increase in intensity when the samples are stored at ambient temperatures. These signals are attributed to hydrolysis products. A doublet and a multiplet in the ranges -62 ± 2 p.p.m. and $+145 \pm 2$ p.p.m. respectively (rel. to CCl_3F), both with coupling constants of 58 Hz and satellite peaks from $^{183}W - ^{19}F$ coupling of 70 ± 1 and 50 ± 1 Hz respectively, are the most prominent of these signals. The multiplet at +145 p.p.m. consists of

nine lines with the correct binomial intensity distribution for a nonet, viz. 1:7:28:56:70:56:28:7:1, and the doublet-nonet intensity ratio is ca. 8.5:1. (These observations were made by Dr. Wm. McFarlane, Sir John Cass College, London, using a sample prepared in this work.[95]) However, in most of the spectra containing this multiplet only five or seven of the main lines are resolved. These parameters are similar to those of the unidentified decomposition products of complexes of WF_6 reported by Tebbe and Muetterties,[35] though there are some discrepancies in the values of the coupling constants.

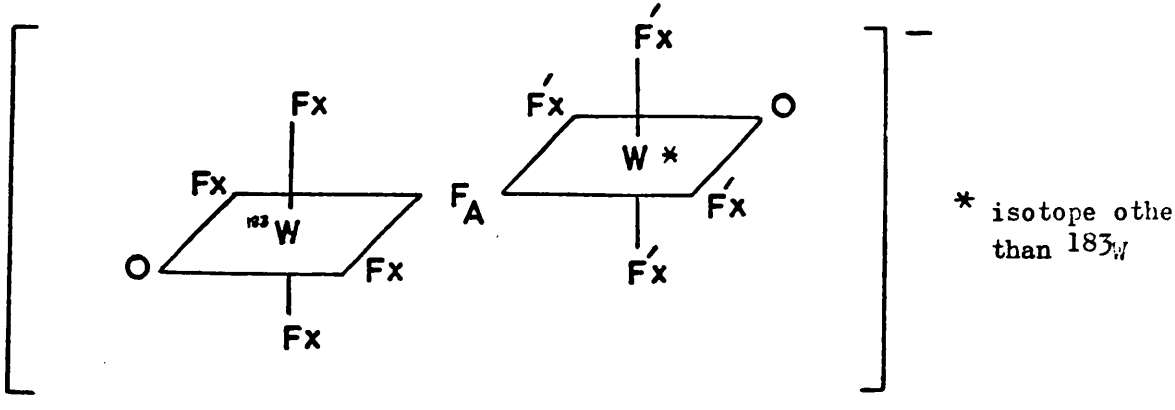
The signals described in the preceeding paragraph are characteristic of an AX_8 spin system, and could arise from the dimeric species $(OF_4W—F—WF_4O)^-$, in which there is a bridging fluorine atom. The species is tentatively formulated as the μ-fluorobis[oxotetrafluorotungstate(VI)] anion (II):



(II)

The ion (II) with octahedral coordination around the tungsten atoms, and a linear W-F-W system, has fluorine atoms in two environments. The bridging fluorine atom, F_A, is spin-coupled equally with the eight terminal fluorine atoms, F_X, giving rise to a nonet, and the eight terminal fluorine atoms are spin-coupled with the bridging fluorine atom, giving rise to a doublet. The resonance of the bridging fluorine atom is at much higher field than that of the terminal fluorine atoms. The present work has yielded no information about the nature of the cationic species, which will vary according to the nature of the derivative of WF_6 from which it is formed, and about the extent of cation-anion association.

The following observation[95] is consistent with the above formulation of this hydrolysis product. The ^{183}W - ^{19}F satellite peaks of the doublet show quintet fine structure, but the main lines do not. The fine structure of the satellite peaks arises from long range F_X - F'_X coupling in the ion (III):



(III)

The presence of only one ^{183}W isotope in (III) produces a $X_4ZAX'_4$ system (Z = ^{183}W) and renders the terminal fluorines magnetically non-equivalent. The main lines arise mainly from magnetically equivalent sets of terminal fluorine atoms in ions which contain tungsten isotopes other than ^{183}W. The lines of the F'_X doublet from ion (III), however, are expected to show fine structure from $F'_X - F_X$ coupling, but this is not resolved as the relative abundance of (III) is low, and the lines are obscured by the more intense lines from the ions which do not contain ^{183}W isotopes. The ^{19}F n.m.r. spectrum of $W_2O_2F_9^-$ is further discussed in chapter 4, and the species appears as a product in some of the reactions described in chapter 2.

The analogous fluorine-bridged, dimeric anions $Sb_2F_{11}^-$ [96] and $As_2F_{11}^-$, [97] have been so formulated on the basis of ^{19}F n.m.r. spectra which are similar to that of $W_2O_2F_9^-$. Crystal structure analyses have confirmed the presence of fluorine bridges in the Nb_2F_{11} and Sb_2F_{11} units of the compounds $SeF_4,2NbF_5$ [98] and $XeF_2,2SbF_5$. [99]

In some cases the ^{19}F n.m.r. spectra of the adducts of WF_6 showed single line resonances in the range -65 ± 5 p.p.m. (rel. to CCl_3F), with satellite peaks from $^{183}W - ^{19}F$ coupling of 70 ± 1 Hz, and these are also assigned to hydrolysis products. The similarity of the spectral parameters to those of WOF_4 and $WOF_4.OMe_2$ (Table 1.3) indicates that these signals arise from WOF_4 species.

The present work and that of Muetterties and Tebbe[35] indicate that

derivatives of WF_6 react with trace amounts of moisture to yield WOF_4, WOF_5^- and $W_2O_2F_9^-$. The origin of $W_2O_2F_9^-$ is uncertain, but a reaction between WOF_5^- and WOF_4 seems feasible:

$$WOF_5^- + WOF_4 \rightleftharpoons W_2O_2F_9^- \qquad (1.5)$$

This is formulated as a reversible process, as the products obtained appear to depend on the solvent in which the hydrolysis is taking place. In acetonitrile and sulphur dioxide, the position of the equilibrium may lie to the left hand side of 1.5. A reaction similar to 1.5 has been observed between AsF_5 and AsF_6^- yielding $As_2F_{11}^-$.[97]

Conclusions

The Raman spectroscopic study of coloured solutions of WF_6 in benzene and acetonitrile leads to the conclusion that the octahedral symmetry of WF_6 is preserved and that the extent of donor-acceptor interaction is small. The experiments aimed at the preparation of a solid donor-acceptor complex of WF_6 with 1-methylnaphthalene and 9-methylanthracene are inconclusive, and further study of these systems seems desirable. Further study of the reaction conditions necessary for the reduction of WF_6 to WF_4 by benzene is also necessary.

Nitromethane is a convenient solvent for the preparation of the complex fluorides $R_4N^+WF_6^-$ (R = ^{n}Bu, ^{n}Pr) by the reaction of WF_6 with the appropriate tetraalkyl ammonium iodide. The large splittings of the infrared-active vibrations of the WF_6^- ion in these complex fluorides provides an interesting spectroscopic problem for future work.

The formation of complexes of WOF_4 in the reactions of WF_6 with dialkyl ethers is to be contrasted with the formation of donor-acceptor complexes of WF_6 with thioethers and selenoethers, and gives some indication of the stability associated with a tungsten-oxygen multiple bond. Spectroscopic evidence points to a monomeric, octahedral structure for $WOF_4.OMe_2$ with the dimethyl ether ligand in a position trans to the terminal oxygen atom. $WOF_4.OMe_2$ may be a useful starting material for explorations of the chemistry of WOF_4.

A product of the hydrolysis of WF_6 derivatives is formulated as the $W_2O_2F_9^-$ anion, and this is thought to arise from the reaction of WOF_5^- with WOF_4. Experiments aimed at the preparation of authentic samples containing $W_2O_2F_9^-$ might be undertaken (e.g. the reaction of $^nPr_4N^+WOF_5^-$ with $WOF_4.OMe_2$) with a view to obtaining more information about this species. The possibility of the preparation of higher polymeric ions ought to be examined.

EXPERIMENTAL SECTION

Chemicals

WF_6, prepared by reaction of tungsten with fluorine,[25, 26] or obtained from Allied Chemical Co., was purified by trap to trap distillation at -80° over NaF. Analar or spectroscopic grade solvents and reactants were used where available; others were purified by literature methods.[100] Dimethyl ether (Air Products), diethyl ether, cyclopentane (B.D.H.), and benzene were dried over sodium wire, and vacuum distilled at low temperatures. Dimethyl sulphide, diethyl sulphide (B.D.H.), dimethyl selenide, diethyl selenide (Emanuel) and diisopropyl sulphide (Aldrich) were dried over lithium aluminium hydride, degassed, and vacuum distilled at low temperatures. Deuteroacetonitrile, deuterochloroform (Ciba), dimethyl disulphide (B.D.H.), acetonitrile, carbon tetrachloride, and nitromethane were dried over P_2O_5, degassed, and vacuum distilled at low temperatures. 1-methylnaphthalene was distilled from sodium wire at 70° (10^{-1} mm). All solvents were stored over activated Linde 4A molecular sieves. 9-methylanthracene, tetra-n-butyl ammonium iodide, and tetra-n-propyl ammonium iodide were degassed for several hours (10^{-4} mm) before use. Tetraethyl ammonium chloride (monohydrate, B.D.H.) was heated in vacuum at 180° (4 hours) to remove water of crystallisation.

Experimental procedures

All manipulations were carried out under high vacuum, and great precautions were taken to exclude trace amounts of moisture.

Samples for Raman spectra were sealed in home-made pyrex cells. Two models - L and T shaped - were used. Both had volumes ca. 0.5 ml, and had near optically flat windows. The T shaped model gave better spectra. The spectra were recorded on a Coderg PH 1 spectrometer with a 50 mW He-Ne laser by Dr. H.J. Clase, formerly of the University of Sussex.

Glass vessels or stainless-steel bombs as appropriate were used for reactions of WF_6. Reactants were condensed into the vessels cooled in liquid nitrogen. Involatile reactants and products were handled in a dry-box.

Details of apparatus and instrumentation are given in the Appendix.

Raman Spectra of WF_6 in benzene, acetonitrile and cyclopentane

The concentrations of the solutions were not determined accurately, but were approximately 1 M w.r.t. WF_6. The results are summarised in Table 1.1.

Tungsten hexafluoride and 1-methylnaphthalene

A bright red solution was obtained when WF_6 (4 g) dissolved in 1-methylnaphthalene (20 ml) at 20°. A small quantity of a dark red solid separated after several days, but could not be isolated

because of the involatility of 1-methylnaphthalene at 20°. When the solution was heated to 80°, a black sticky solid, which contained tungsten, was obtained.

Tungsten hexafluoride and 9-methylanthracene

WF_6 (2 g, 6.7 mmoles) and 9-methylanthracene (0.7 g, 3.6 mmoles) in CCl_4 (10 ml) produced a dark green solution at 20°. On removal of the solvent and unreacted WF_6 a dark green solid was obtained. Elemental analysis (two samples, from separate experiments). Found: C, 89.9, 75.7; H, 6.1, 5.44; F, 0.0, 1.74%. 9-methylanthracene, $C_{15}H_{12}$, requires: C, 93.7; H, 6.3%.

The solid fumed slightly in air, but did not react with water. It was extracted into CCl_4, and a yellow solution was obtained. The infrared spectrum of the yellow solid recovered after removal of the CCl_4 was identical to that of 9-methylanthracene, and t.l.c. analysis showed that only one compound was present. The infrared spectrum of the dark green solid (nujol mull) contained an absorption at 762 cm^{-1} in addition to those characteristic of 9-methylanthracene.

Tungsten hexafluoride and benzene

WF_6 (5 g, 17 mmoles) and C_6H_6 (4 g, 51 mmoles) were allowed to react in a stainless-steel bomb at 115° for 10 days. The volatile material was identified from its infrared spectrum as a mixture of

WF_6,[101] C_6H_6,[102] and SiF_4[103] (trace). There was no solid residue in the bomb.

Tungsten hexafluoride and tetra-n-butyl ammonium iodide

WF_6 formed a pale yellow, stable solution in nitromethane. WF_6 (4 g, 13.5 mmoles) was condensed into a glass reaction vessel containing $^nBu_4NI$ (1.4 g, 3.8 mmoles) in nitromethane (20 ml). Reaction occured at 20°, and iodine was released. After 12 hours the volatile materials (unreacted WF_6, CH_3NO_2 and I_2) were removed at 20°, and the reaction flask was heated to 70° (24 hours) to ensure complete removal of I_2. The unreacted WF_6 in the volatile materials was hydrolysed to WO_3 by addition of H_2O. The I_2 was extracted into CCl_4, and titrated with standard $Na_2S_2O_3$. The amount of I_2 recovered was 0.45 g, 1.8 mmoles, indicating that reaction had gone to completion.

A golden brown solid (2.3 g) remained in the reaction flask. Elemental analysis. Found: C, 31.0; H, 5.56; F, 24.8; N, 3.29; W, 35.1%. $C_{16}H_{36}F_6NW$ requires: C, 35.6; H, 6.71; F, 21.1; N, 2.60; W, 34.0%.

The infrared spectrum of this product was recorded from 4000 - 100 cm^{-1}. Absorptions characteristic of the $^nBu_4N^+$ ion were assigned by comparison with the spectrum of $^nBu_4NI$. The following additional absorptions were observed: 700w, 675w, 650s, 615s, 518m, 285wbr, 248m cm^{-1}. Conductivity data was obtained as follows:

in CH_3NO_2, Λ = 99.8 (8×10^{-4}M), 89.8 (3×10^{-3}M) ohm^{-1} cm^2; in CH_3CN, Λ = 123.6 (4×10^{-3}M) ohm^{-1} cm^2. The equivalent conductivity of $^nBu_4NI$ in CH_3CN was, Λ = 181 ohm^{-1} cm^2 (4×10^{-3}M).

The u.v. spectrum of the product (800-300mμ) was recorded in CH_3CN (4×10^{-3}M), and consisted of an absorption of low intensity (ϵ=100) at 315mμ (31,750 cm^{-1}).

The concentrations of the solutions for conductivity measurements and u.v. spectra were determined spectrophotometrically.[104]

Tungsten hexafluoride and tetra-n-propyl ammonium iodide

The experimental procedure was the same as for WF_6 and $^nBu_4NI$.

WF_6 (4 g, 13.5 mmoles) and $^nPr_4NI$ (1.1 g, 3.5 mmoles) in nitromethane (15 ml) yielded I_2 (0.44 g, 1.7 mmoles) and a golden brown solid (2.0 g).

Elemental analysis. Found: C, 26.0; H, 5.40; F, 23.7; N, 3.36; W, 37.5%. $C_{12}H_{28}F_6NW$ requires: C, 29.8; H, 5.83; F, 23.5; N, 2.89; W, 38.0%.

The infrared spectrum of the product (4000 - 100 cm^{-1}) contained the following absorptions in addition to those characteristic of the $^nPr_4N^+$ ion: 1018sh, 1016m, 701m, 678m, 625s, 605s, 513m, 330m, 284m, 275sh, 250s, 236m cm^{-1}.

The u.v. spectrum of the product (800-300mμ) was recorded in CH_3CN (6.5×10^{-4}M), and consisted of an absorption at 308mμ (32470 cm^{-1}) (ϵ = 130).

Tungsten hexafluoride and dimethyl ether

(a) WF_6 (4.0 g, 13 mmoles) and Me_2O (3.3 g, 72 mmoles) were allowed to react in a stainless-steel bomb at 110° for 65 hours. The volatile products were two immiscible, colourless liquids at 20°, and the absence of the characteristic yellow colour of a WF_6 - Me_2O mixture indicated that the reaction had gone to completion.

The fraction volatile at -80° was identified from its infrared spectrum as a mixture of Me_2O,[105] MeF,[105] and SiF_4[103] (trace).

The fraction volatile at 25°, a colourless liquid, m.p. ca. 10°, was identified as oxotetrafluoro(dimethyl ether)tungsten(VI), $WOF_4.OMe_2$, (2.5 g, 8 mmole, yield 60%).

Elemental analysis. Found: C, 7.55; H, 2.18; F, 23.5; W, 54.4%. $C_2H_6F_4O_2W$ requires: C, 7.46; H, 1.88; F, 23.6; W, 57.1%.

Infrared spectrum (liquid film, 4000 - 400 cm^{-1}): 2950m, 2890sh, 2845m, 2035w, 1530mbr, 1450m, 1320sh, 1255m, 1156s, 1045sh, 1025s, 883s, 853m, 815s, 700s, 667sh, 640s, 456m cm^{-1}.

Mass spectrum (electron beam 70 eV, cold inlet; $^m/e$ values correspond to the ^{186}W isotope): $^m/e$ = 278, WF_4O^+; 259, WF_3O^+; 243, WF_3^+; 240, WF_2O^+; 224, WF_2^+; 221, WFO^+; 205, WF^+; 202, WO^+; 186, W^+; and other ions characteristic of Me_2O. The tungsten-containing ions were identified by their characteristic isotope patterns, though in some cases these overlapped.

The ^{19}F n.m.r. spectrum (neat liquid, CCl_3F ref.) consisted of a major signal at -62.8 p.p.m. (single line, J_{WF} = 68 Hz) and signals of less intensity (5% of total) at -60.3 p.p.m. (doublet, J_{FF} = 58 Hz, J_{WF} = 72 Hz) and +146.0 p.p.m. (multiplet, minimum of 7 lines, J_{FF} = 58 Hz, J_{WF} = 51 Hz). The doublet and multiplet had relative intensities ca. 8:1, and the intensity of these signals had increased greatly (to 50% of total) in a spectrum re-run after 7 days. The ^1H n.m.r. spectrum consisted of a major signal at 6.31 τ (single line) and a weak signal at 6.41 τ (single line).

This product reacted vigorously with NaF and Et_4NCl with evolution of Me_2O, and formation of a white and a pale yellow solid respectively.

The involatile product, a small quantity of black lustrous solid, was not investigated, and was identical in appearance to the involatile product in (c).

(b) Reaction of WF_6 (15 g, 50 mmole) and Me_2O (2 g, 44 mmoles) in a stainless-steel bomb at 120° (110 hours) gave as a major product a brown involatile solid, which hydrolysed rapidly on exposure to the atmosphere. Elemental analysis gave, W, 58.2%.

(c) WF_6 (3 g, 10 mmoles) and Me_2O (5 g, 110 mmoles) were allowed to react in a stainless-steel bomb at 25° for 48 hours. The volatile material was a mixture of Me_2O, WF_6 and SiF_4 (trace) (identified by i.r.[105, 101, 103]).

The involatile product was a black lustrous solid. Elemental analysis. Found: C, 4.28; H, 2.55; F, 1.19; W, 53.8%. Infrared spectrum (nujol and florube mulls, 4000 - 400 cm^{-1}): 3058w, 2930w, 2850w, 1460m, 1255w, 1160wbr, 1075m, 1025s, 980w, 956m, 924s, 870w, 845w, 830w, 770sh, 745m, 734sh, 704s, 670sh, 659sh, 640s, 592sh cm^{-1}.

Oxidation state determinations on this product using $FeSO_4$ and $K_2Cr_2O_7$ did not give reproducible results, but indicated that the oxidation number of tungsten was less than 6.

Tungsten hexafluoride and diethyl ether[107]

(a) A solution of WF_6 (4 g, 13.5 mmoles) in Et_2O (7 g, 94 mmoles) was yellow when freshly prepared. After several hours a small quantity of black solid had separated, and after several weeks a few drops of a colourless, viscous liquid had also separated.

WF_6 and Et_2O were removed at -20°. The colourless liquid product was volatile at 25°, but elemental analyses performed on several samples prepared in this way did not give consistent results (e.g. found: C, 30.7; H, 3.37; F, 15.9, 21.0; W, 42.5, 52.5%. $WOF_4.OEt_2$ requires: C, 13.7; H, 2.88; F, 21.7; W, 52.5%). Its infrared spectrum (liquid film, 4000 - 400 cm^{-1}) was similar to that of $WOF_4.OMe_2$, and was as follows: 2985m, 2940m, 2910m, 1520m, 1442m, 1387m, 1192m, 1107w, 1012s, 940w, 897m, 750m, 698m, 642s, 609sh cm^{-1}. Elemental analyses performed on samples of the black, involatile

solid residue from separate preparations did not give consistent results (e.g. found: F, 21.6; W, 48.8, 52.5, 48.1%).
Infrared spectrum (nujol and florube mulls, 4000 - 400 cm^{-1}): 2920w, 1014m, 970s, 858s, 795s, 723m, 645s, 606s cm^{-1}.

Oxidation state titrations using $FeSO_4$ and $K_2Cr_2O_7$ indicated that the oxidation state of tungsten was less than 6.

(b) WF_6 (4 g, 13.5 mmoles) and Et_2O (3.6 g, 48 mmoles) were allowed to react in a stainless-steel bomb at 80° for 12 days. The volatile products were two immiscible liquids at 20°, and the absence of the characteristic yellow colour of a WF_6 - Et_2O mixture indicated that the reaction had gone to completion.

The infrared spectrum of the fraction volatile at -20° was identical to that of Et_2O.[102]

The fraction volatile at 25° was a colourless liquid (1 ml), m.p. ca. 20°, which rapidly decomposed at 20°, depositing a white solid. It reacted vigorously with NaF with evolution of Et_2O. Elemental analysis of a partially decomposed sample gave: C, 17.9; H, 6.89; F, 16.6%. The infrared spectrum was very similar to that of the liquid product obtained in (a).

The involatile product was a small quantity of black lustrous solid. Elemental analysis gave: F, 15.2; W, 66.4%

Tungsten hexafluoride and dimethyl sulphide

A mixture of WF_6 (1 g, 3.4 mmoles) and Me_2S (1.7 g, 27 mmoles)

was allowed to react at 20° in a glass vessel. The mixture was dark brown, and after 24 hours some pale yellow solid had separated. This solid sublimed slowly at 70°, with some decomposition to WF_6 and Me_2S (identified by i.r.[101, 106]). The sublimate, a white solid, decomposed on standing for several hours, yielding a dark brown solid, which was not characterised. The ^{19}F n.m.r. spectrum (CH_3CN solution, CCl_3F ref.) consisted of a single line at -142.3 p.p.m.

The yellow-brown, involatile residue left after sublimation of the solid obtained originally was not identified. Partial elemental analysis gave: C, 8.77; H, 2.58; S, 9.06; F, 8.43%. Infrared spectrum (nujol and florube mulls, 4000 - 400 cm^{-1}): 3030w, 2945w, 1048m, 1022s, 980m, 942w, 702m, 678sh, 669sh, 638sbr, 590sbr, 502mbr. cm^{-1}.

Tungsten hexafluoride and diethyl sulphide

A mixture of WF_6 (4 g, 13.5 mmoles) and Et_2S (8.4 g, 93 mmoles) was allowed to react at 20° in a glass vessel. The mixture was initially dark brown. Reaction was complete after 20 days, yielding two immiscible layers. The colourless upper layer was volatile at 20°, and was identified as unreacted Et_2S (by i.r.[106]).

The lower layer was a pale yellow, viscous liquid, involatile at 20°. It distilled slowly at 50°, with some decomposition into WF_6 and Et_2S (identified by i.r.[101, 106]), and was identified as

hexafluorobis(diethyl sulphide)tungsten(VI), $WF_6(Et_2S)_2$. This product dissociated slightly at 20°, and hydrolysed immediately in water producing a transient purple colour and WO_3.

Elemental analysis. Found: C, 19.7; H, 3.76; F, 23.5; S, 13.3; W, 38.2%. $C_8H_{20}F_6S_2W$ requires: C, 20.1; H, 4.22; F, 23.8; S, 13.4; W, 38.5%.

Infrared spectrum (liquid film, 4000 - 600 cm^{-1}): 2980s, 2935m, 2870w, 1465sh, 1455s, 1425s, 1390s, 1280s, 1260sh, 1087m, 1045w, 1020s, 975s, 790m, 765sh, 698m, 672sh, 648s, 613s cm^{-1}.

The ^{19}F n.m.r. spectrum (neat liquid, CCl_3F ref.) consisted of a single resonance at -70.8 p.p.m. ($\frac{1}{2}$ height width = 12 Hz). No ^{183}W - ^{19}F satellite peaks were observed. The ^1H n.m.r. spectrum (externally referenced; chemical shifts, $\pm$ 0.1τ, are mid-points of resonances) consisted of two multiplets at 6.8 τ (minimum of 4 lines, J = 7 Hz) and 8.5 τ (minimum of 5 lines) with relative intensities 2:3. A similar ^1H n.m.r. spectrum was obtained at 100 MHz. After several days the ^{19}F n.m.r. spectrum contained an additional signal at -62.1 p.p.m. (doublet, J_{FF} = 57 Hz, J_{WF} = 72 Hz).

The ^{19}F n.m.r. spectrum of the complex in CH_3CN (CCl_3F ref.) consisted of signals at -67.3 p.p.m. (single line) and -62.0 p.p.m. (doublet, J_{FF} = 59 Hz).

Reproducible ^{19}F n.m.r. resonances which could be assigned to

the complex were not obtained. In some experiments, particularly with neat liquid samples, no resonances were observed; in others, only those characteristic of the hydrolysis products WOF_4 and $W_2O_2F_9^-$ (Table 1.3) were observed.

$WF_6(Et_2S)_2$ was insoluble in Et_2O, and decomposed ca. 100° yielding a black intractable tar.

Tungsten hexafluoride and diisopropyl sulphide

WF_6 (3 g, 10 mmoles) and $^iPr_2S$ (3 g, 25.5 mmoles) were allowed to react at 20° for 12 days in a glass vessel. The mixture was initially purple. After removal of unreacted WF_6 and $^iPr_2S$ at 20°, a few drops of a colourless, involatile liquid remained. This product was soluble in CD_3CN yielding a purple solution, and the ^{19}F n.m.r. spectrum (CCl_3F ref.) consisted of signals at -66.6 p.p.m. (single line, J_{WF} = 69 Hz), -61.4 p.p.m. (doublet, J_{FF} = 59 Hz, J_{WF} = 72 Hz) and +145.0 p.p.m. (multiplet, minimum of 5 lines, J_{FF} = 59 Hz, J_{WF} = 49 Hz). The relative intensities of the doublet and multiplet were ca. 8:1.

Tungsten hexafluoride and dimethyl disulphide

WF_6 (4 g, 13.5 mmoles) and Me_2S_2 (4 g, 42.5 mmoles) were allowed to react at 20° for 5 days in a glass vessel. The mixture was initially dark brown. After removal of unreacted WF_6 and Me_2S_2 at 20°, a pale brown, involatile solid remained.

Elemental analysis (F not obtained). Found: C, 8.04; H, 1.71;

S, 21.7; W, 43.8%. WF_6,1.5 Me_2S_2 requires: C, 8.29; H, 1.04; S, 22.1; W, 42.3%.

This product was sparingly soluble in $CDCl_3$, and the ^{19}F n.m.r. spectrum (CCl_3F ref.) consisted of signals at -85.0 p.p.m. (broad resonance, $\frac{1}{2}$ height width ca. 100 Hz), -63.7 p.p.m. (doublet, J_{FF} = 58 Hz, J_{WF} = 72 Hz), -1.0 p.p.m. (single line), +144.1 p.p.m. (multiplet, minimum of 7 lines, J_{FF} = 59 Hz).

Tungsten hexafluoride and dimethyl selenide

WF_6 (5 g, 17 mmoles) and Me_2Se (5 g, 46 mmoles) were allowed to react at 20° for 2 hours in a glass vessel. A red solid was formed initially, and after removal of unreacted WF_6 and Me_2Se at 20°, a yellow solid remained, which darkened rapidly and was not identified.

Tungsten hexafluoride and diethyl selenide

WF_6 (2 g, 6.7 mmoles) and Et_2Se (3 g, 22 mmoles) reacted vigorously at 20° to yield two immiscible liquids. The reaction was complete in 10 minutes. The upper layer was colourless, and was identified as unreacted Et_2Se (by i.r.). The lower layer was a bright orange, involatile, viscous liquid, identified as hexafluorobis(diethyl selenide)tungsten(VI), $WF_6(Et_2Se)_2$.

Elemental analysis. Found: C, 16.7; H, 3.42; F, 19.6; W, 32.8%. $C_8H_{20}F_6Se_2W$ requires: C, 16.8; H, 3.52; F, 19.9; W, 32.2%.

Infrared spectrum (liquid film, 4000 - 400 cm^{-1}): 2985s, 2940m,

2880m, 1450s, 1425s, 1390s, 1260s, 1230sbr, 1055m, 1010s, 970s, 760m, 703s, 680w, 669m, 615s, 570s, 490wbr cm^{-1}, Raman spectrum (neat liquid): 2980w, 2963w, 2941m, 2884w, 2830w, 2757w, 1452w, 1422w, 1386w, 1969wsh, 1452m, 1420m, 1386w, 1269w, 1241m, 1065m, 1050w, 1021w, 962m, 689s, 571sh, 541s, 300m, 281w, 253m, 207w, 159w cm^{-1} (all the lines were polarised).

$WF_6(Et_2Se)_2$ dissociated slightly on standing at 20°.

The ^{19}F n.m.r. spectrum (neat liquid, CCl_3F ref.) consisted of a major signal at -143.6 p.p.m. (single line, $\frac{1}{2}$ height width = 8 Hz, ^{183}W - ^{19}F satellite peaks not observed) and minor signals at -64.1 p.p.m. (doublet, J = 54 Hz) and -61.6 p.p.m. (doublet, J = 57 Hz). The ^{1}H n.m.r. spectrum (externally referenced; chemical shifts, $\pm$ 0.1τ, are mid-points of resonances) consisted of two multiplets at 6.8τ (minimum 7 lines) and 8.5τ (minimum 5 lines) with relative intensities 2:3. A similar spectrum was obtained at 100 MHz, and the spectrum did not simplyfy to that of an A_3B_2 system at 100°.

The ^{19}F n.m.r. spectrum of a solution of $WF_6(Et_2Se)_2$ in CH_3CN(CCl_3F ref.) consisted of a doublet at -63.9 p.p.m. (J = 58 Hz). Similar difficulties of reproducibility of the ^{19}F n.m.r. spectra were encountered as for $WF_6(Et_2S)_2$.

CHAPTER TWO

THE FLUORINATION OF SOME OXYGEN-CONTAINING COMPOUNDS OF SULPHUR AND PHOSPHORUS WITH TUNGSTEN HEXAFLUORIDE.

PREPARATION AND REACTIONS OF ALKOXY AND PHENOXY TUNGSTEN(VI) PENTAFLUORIDES

Introduction

The interaction of WF_6 with oxygen-containing compounds of sulphur and phosphorus has received little attention. Clark and Emeléus[33] observed a slow reaction between WF_6 and sulphur dioxide at ambient temperatures, yielding thionyl fluoride and tungsten oxotetrafluoride. With WF_6 and sulphur trioxide they obtained the involatile compound $WF_6,4.5SO_3$, formulated as the fluorosulphate $WF_2(SO_3F)_4$, the discrepancy in the analytical figures being attributed to the difficulty of removing excess SO_3. Preliminary investigations carried out in these laboratories indicated that WF_6 reacts at ambient temperatures with dimethyl sulphoxide and dimethyl sulphite, but not with dimethyl sulphate up to 60^o,[108] and that a complex reaction, involving substituent exchange, occurs between WF_6 and trimethyl phosphite at low temperatures.[109]

This chapter describes a detailed investigation of the interaction of WF_6 with dimethyl sulphoxide, dimethyl, diethyl and diphenyl sulphites, dimethyl sulphone, sulphur trioxide, trimethyl phosphite, dimethyl phosphite and dimethyl methylphosphonate. These reactions were undertaken with a view to examining the action of WF_6 on S-O, S=O, P-O and P=O bonds, and the nature of the tungsten-containing species formed. The reinvestigation of the reaction of WF_6 with SO_3 was undertaken with a view to the preparation and ^{19}F n.m.r. spectral characterisation of the series of fluorosulphates $WF_{6-n}(SO_3F)_n$. Such compounds are of interest as their physical and chemical properties are usually very different from those of the binary fluorides from which they are derived.[110] Preliminary accounts of some of the work described in this chapter have been published,[111, 112] and the work has recently been extended to reactions of WF_6 with cyclic sulphite esters and sultones.[113]

Related systems have received some attention. Clark and Emeléus have studied the interaction of the Group Va pentafluorides with SO_2 and SO_3.[114] At ambient temperatures VF_5 reacts quantitatively with SO_2 to yield SOF_2, and reacts readily with SO_3 to yield pyrosulphuryl fluoride:

$$VF_5 + SO_2 \longrightarrow VOF_3 + SOF_2$$

$$VF_5 + 2SO_3 \longrightarrow VOF_3 + S_2O_5F_2$$

NbF_5 does not react with SO_2, but both NbF_5 and TaF_5 react with SO_3 to yield the compounds $NbF_5, 2.1SO_3$ and $TaF_5, 2.6SO_3$ respectively.

These are formulated as the fluorosulphates $NbF_3(SO_3F)_2$ and $TaF_3(SO_3F)_2$, from which excess SO_3 has not been completely removed. Thermal decomposition of the niobium and tantalum compounds yields, unexpectedly, sulphuryl fluoride, SO_2F_2, not $S_2O_5F_2$.

A large number of sulphoxide adducts of both metal and non-metal halides have been described,[115] and among the binary fluorides for which dimethyl sulphoxide (DMSO) adducts have been prepared are BF_3,[116, 117] SbF_3,[34] SiF_4,[118, 119, 120] GeF_4,[119] SnF_4,[119] TiF_4,[119] ZrF_4,[119] MoF_4,[119] NbF_5,[121] and TaF_5.[121] A sulphoxide can co-ordinate either via the sulphur or the oxygen atom. Cotton and co-workers[116, 122] have suggested that these possibilities can be distinguished by the direction of the shift of the SO stretching frequency of the sulphoxide on coordination. Coordination via the oxygen atom is expected to decrease the SO bond order, and cause the SO stretching frequency to shift to lower energy, whereas coordination via the sulphur atom is expected to have the opposite effect. In an infrared study of a number of complexes containing DMSO, they observed shifts of the SO stretching frequency in both directions. In most cases the shifts were to lower frequency, implying coordination via oxygen. Only for platinum(II) and palladium(II) complexes were shifts of the SO stretching frequency to higher energy recorded, implying coordination via sulphur. $d\pi - d\pi$ back-bonding from filled metal d-orbitals to vacant sulphur

d-orbitals may be a factor influencing this arrangement.

Drago and Meek[123] have also observed shifts of the SO stretching frequency to lower energy in complexes containing DMSO, but they disagree with Cotton and co-workers as to the assignments of the SO stretch and the methyl rocking frequency. Similar results have been obtained for complexes containing tetrahydrothiophene oxide,[124] diphenyl sulphoxide,[125, 126] and mixed alkyl-aryl sulphoxides.[127]

Several crystal structure determinations of complexes with sulphoxide ligands have been carried out, and these confirm the general conclusions drawn from infrared studies. It has been demonstrated that in BF_3.DMSO, $SbCl_5.Ph_2SO$, $SnCl_4$.2DMSO,[115] and trans-$[FeCl_2(DMSO)_4][FeCl_4]$[128] coordination of the sulphoxides is via oxygen, whereas in $PdCl_2$.2DMSO[128] coordination is via sulphur.

Cotton and co-workers[116] were unable to isolate an adduct of boron trichloride with DMSO, and Lappert and Smith[120] later showed that reaction occurs to yield a chloro-substituted sulphide, the oxygen of the sulphoxide group being abstracted by boron to form the unstable boron oxochloride, BOCl (formulated as the boroxole, $(ClBO)_3$[129]). The reaction is formulated as:

$$Me_2SO + BCl_3 \longrightarrow MeS.CH_2Cl + \tfrac{1}{3}(BOCl)_3 + HCl$$

$$MeS.CH_2Cl + \tfrac{1}{3}(BOCl)_3 \longrightarrow MeS.CH_2Cl,BOCl$$

$$MeS.CH_2Cl + BCl_3 \longrightarrow MeS.CH_2Cl,BCl_3 .$$

Similar reactions are reported for silicon tetrachloride with dimethyl and diphenyl sulphoxides.

Oxygen abstration from DMSO by molybdenum pentachloride[130] and vanadium trichloride[131] has been reported. In the former case, the complex $MoOCl_3.2DMSO$ is formed; in the latter, vanadium is oxidised to the +IV state to yield $VOCl_2.3DMSO$. Niobium and tantalum pentachlorides and pentabromides abstract the oxygen atom from dimethyl and diphenyl sulphoxides to yield the corresponding polymeric oxohalide and halogen substituted sulphide, together with coordination of further molecules of sulphoxide to the oxohalide.[132] In the case of $NbCl_5$, the process is limited to the substitution of two of the halogen atoms of the halide:

$$NbCl_5 + 3Me_2SO \rightarrow NbOCl_3.2Me_2SO + Me_2SCl_2$$

$$Me_2SCl_2 \rightarrow ClCH_2SMe + HCl .$$

Further substitution of halogen by oxygen occurs with $NbBr_5$, $TaCl_5$ and $TaBr_5$, with attendant increase of polymerisation through oxygen-bridging to yield species with the empirical formulae, $Ta_3O_4Cl_7(Me_2SO)_5$, $Nb_4Br_8O_6(Me_2SO)_8$, $Nb_4Br_3O_6(Me_2SO)_6$, $Ta_2BrO_5(Me_2SO)_3$, and $TaO_2Br.Ph_2SO$. This behaviour is in contrast to that of NbF_5 and TaF_5 which yield stable 1:2 adducts with DMSO.[121]

There are few reports of complexes with sulphite esters and sulphones as ligands. From a study of the relative stabilities of

1:1 adducts of BF_3, Laughlin[117] has obtained evidence that in the series R-S-R, R.SO.R and $R.SO_2.R$ ($R = nC_{12}H_{25}$, R = Me, Et) the sulphoxide is considerably more basic than either the sulphide or the sulphone. These results are in agreement with the earlier observation of Wimer that diethyl sulphite is much less basic than a sulphoxide.[133]

Gutmann and Scherhaufer[134] have recently suggested that ethylene sulphite is a weak donor to cobalt(II). Van Leewen and Groeneveld[135] have prepared complexes of nickel(II) and cobalt(II) with trimethylene sulphite, and found that the latter is readily displaced by other ligands. They also conclude that sulphites are much weaker donors than sulphoxides.

Complexes with phosphite esters as ligands are well documented,[136] and the formation of a 1:1 complex is the first step in the complex reaction between trimethyl phosphite and phosphorus pentafluoride.[137] Phosphorus(III) compounds containing >POR groups readily undergo Michaelis-Arbusov rearrangements[138] to phosphorus(V) compounds containing >P(O)R groups, and the reaction of $P(OMe)_3$ with PF_5[137] has been rationalised on this basis. Some examples of the fluorination of P=O bonds with sulphur tetrafluoride have been reported.[139]

The Reaction of Tungsten Hexafluoride with Dimethyl Sulphoxide

WF_6 and dimethyl sulphoxide react exothermically at 0° to yield a pale yellow viscous oil whose ^{19}F n.m.r. spectrum in CD_3CN (Table 2.6, experimental section) indicates that the $W_2O_2F_9^-$ anion is a major product. Other signals are assigned to WOF_5^- and a complex of WF_6, possibly $WF_6.OSMe_2$, these assignments being made on the basis of the similarity of the spectral parameters to an authentic sample of WOF_5^- (Table 1.3) and other WF_6.donor complexes (Table 1.5) respectively. If the reaction is carried out in glass, a considerable quantity of SiF_4 is produced, suggesting that HF is a reaction product, and extensive hydrolysis complicates the reaction products.

A minor product of reactions in which the mole ratio DMSO : $WF_6 \geqslant 2$ is a colourless, volatile liquid, which decomposes slowly in glass at ambient temperatures. High resolution mass measurements have established the presence of the ions $C_2H_3F_2O^+$, $C_2H_4FO^+$, CH_2F^+ and CH_3O^+ in the mass spectrum of this material, and the product is formulated as bis(monofluoromethyl)ether. The ^1H n.m.r. spectrum is consistent with the second-order pattern calculated for the X_2X_2' part of an $AA'X_2X_2'$ system (where $J_{XX'} = 0$) by Harris,[140] and analysis of the ^1H n.m.r. spectrum by this method yields the following values for the coupling constants: $J_{HF} = 54$, $J_{HF'} = 0.8$, $J_{FF'} = 11$, $J_{HH'} = 0$ Hz. These values are reasonable

for CH_2FOCH_2F by analogy with other hydrofluorocarbon compounds.[141] The ^1H and ^{19}F chemical shifts are 4.88τ and +156.6 p.p.m. (rel. to CCl_3F) respectively, and the spectra indicate that the molecule is symmetrical. A complete analysis of both spectra is being undertaken by Dr. N.M.D. Brown, New University of Ulster, and will be published elsewhere. The infrared spectrum in the region 4000 - 400 cm^{-1} contains absorptions which can be assigned to, ν CH (3010-2860), δ_{CH_2} (1438), δ HCF (1268), ν COC (1192, 1184, 1090) and νCF (1013, 1005).[142] However the ready decomposition of the product at ambient temperatures and its contamination by trace amounts of other unidentified reaction products precludes an unambiguous identification.

CH_2FOCH_2F has been prepared by the reaction of SF_4 with α-polyoxomethylene, $(CH_2O)_x$,[57] sym-trioxane, $(CH_2O)_3$, and DMSO.[143] The physical and spectral properties of these samples are identical to those described above. Lawless and Hennon[144] have reported that the main product from the reaction of IF_5 with DMSO is $CH_2FS(O)H$. The formulation of this compound is based largely on low-resolution mass spectrometric measurements and assignments of infrared and n.m.r. spectra. The physical and spectral data are almost identical to those obtained in the present work, and the formulation of this product as $CH_2FS(O)H$ is open to question.

Reactions of Tungsten Hexafluoride with Sulphite Esters

WF_6 and sulphite esters $(RO)_2SO$, R = Me, Et, Ph react with exchange of RO and F substituents. Equimolar quantities yield the corresponding alkoxy or phenoxy tungsten(VI) pentafluoride and fluorosulphite ester (fluorosulphinate):

$$(RO)_2SO + WF_6 = ROS(O)F + WF_5OR \quad (2.1)$$

The reactions are rapid at -40° (Me, Et) or 20° (Ph), and product yields of 90% or higher are obtained.

Metal salts of the unknown fluorosulphurous acid HSO_2F are well known,[145] but only a few esters derived from this acid had been reported at the commencement of this work.[146, 147] A very recent report deals with the preparation and properties of a series of alkyl fluorosulphites, including MeOS(O)F and EtOS(O)F.[148] The preparative methods are summarised in Table 2.1, and the yields of fluorosulphites obtained in the present work compare favourably with those obtained by other methods. The compounds ROS(O)F, R = Me, Et, Ph are colourless, volatile liquids, which hydrolyse readily in moist air producing HF. The alkylfluorosulphites (R = Me, Et) decompose slowly when heated to yield SO_2 and the corresponding alkyl fluoride,[143] and PhOS(O)F decomposes slowly at ambient temperatures.[147]

The infrared and n.m.r. spectra of the fluorosulphites are summarised in Table 2.2, and these are consistent with their

TABLE 2.1

The Preparation of Fluorosulphite Esters

R	Method of Preparation	Yield of ROS(O)F	Ref.
^{n}Bu; $CH_2CH_2OCH_3$	$ROS(O)Cl + KSO_2F$ (100°)	70-80%	146
Ph	$ROS(O)Cl + NaF/CH_3CN$	85%	147
Me; Et; ^{n}Pr; ^{n}Bu; ^{i}Bu; ^{sec}Bu.	$ROS(O)Cl + KSO_2F$ (40°)	40-75%	148
Me; Et; Ph	$(RO)_2SO + SF_4$ (130°-140°)	90%	111
Me; Et; Ph	$(RO)_2SO + WF_6$ (-40°- 25°)	85-100%[a]	

[a] The value of 40% given in ref. 111 for this reaction is based on a two-fold excess of sulphite initially used.

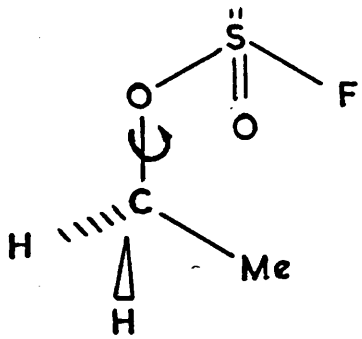
TABLE 2.2

Infrared and N.m.r. spectra of Fluorosulphite Esters and related Cmpds.

Compound	δ_H τ	δ_F (rel. CCl_3F) p.p.m.	J_{HF} Hz	ν(SO) cm^{-1}	ν(SF) cm^{-1}	ν(COS) cm^{-1}	Ref.
MeOS(O)F (neat liquid)	6.15	-55.6	1.3	1266	700		
MeOS(O)F	6.17	-54.7	1.2	1250	680		148
EtOS(O)F (neat liquid)	8.65(Me) 5.65(CH_2)[a]	-59.8	1.3[b]	1260	696		
EtOS(O)F	8.65 5.60, 5.69	-58.6	1.0, 1.5	1250	675		148
PhOS(O)F (neat liquid)	2.9[c]	-64.5[c]		1265			
PhOS(O)F		-62.5		1263		1183	147
$(MeO)_2SO$				1208			150
$(EtO)_2SO$				1206			150
$(PhO)_2SO$				1245			150
SOF_2				1312			150
Me_2SO				1055			151

[a] Two overlapping quartets, separation ~ 1 Hz, each peak further split by $^1H - ^{19}F$ coupling. [b] Average value. [c] The signals showed fine structure, but were not analysed.

formulation, being in good agreement with published values. The S=O stretching modes are readily distinguished, but assignments of the SF stretching modes are less clear as several absorptions occur in this region. The values of the S=O stretching frequencies of the fluorosulphites are approximately midway between those of the corresponding sulphite ester and SOF_2, consistent with the greater electronegativity of fluorine. Correlations of the S=O stretching frequencies in sulphinyl compounds with the electronegativities of substituents have not been as successful as similar correlations for C=O stretching frequencies in carbonyl compounds.[149, 150] This may be accounted for in terms of the non-planarity of sulphinyl compounds, interaction between the p- or π-orbitals of the substituent group and the d-orbitals of sulphur, or coupling of the vibrations. Magnetic non-equivalence of the methylene protons in EtOS(O)F results from the lack of symmetry around the pyramidal sulphur atom with respect to internal rotation about the C-O-S linkage (I), and accounts for the complexity of the ^{1}H n.m.r. spectrum. A similar effect is observed in diethyl sulphite.[152]



(I)

Pentafluoromethoxotungsten(VI), WF_5OMe, is a white, crystalline solid, which sublimes readily at 20° (10^{-4}mm). It hydrolyses readily in moist air, but not as rapidly as WF_6, and decomposes slowly at 20° to give WOF_4 and MeF, significant amounts being formed after seven days. The compound melts ca. 85°, and some decomposition occurs at this temperature. At 135° decomposition is rapid and complete. It is advisable to store WF_5OMe at low temperatures to avoid decomposition.

Pentafluoroethoxotungsten(VI), WF_5OEt, is a pale yellow solid, and is thermally less stable than WF_5OMe. It decomposes rapidly at ambient temperatures to yield ethyl fluoride and presumably WOF_4 by analogy with the decomposition of WF_5OMe. WF_5OEt has not been isolated pure. Pentafluorophenoxotungsten(VI), WF_5OPh, is a dark red solid, m.pt. ca. 80°, which sublimes slowly at 20° and readily at 60° (10^{-4}mm) without decomposition. It is stable up to 180°, at which temperature it attacks glass. Its colour is similar to tungsten hexaphenoxide, $W(OPh)_6$, and its ring substituted derivatives.[153] It does not hydrolyse in moist air as rapidly as WF_5OMe.

Both WF_5OMe and WF_5OPh are soluble in hexafluorobenzene giving pale yellow and dark red solutions respectively. WF_5OMe is also soluble in WF_6, and sparingly soluble in CCl_3F, but reactions occur with benzene and acetonitrile (see below). Typical ^1H and ^{19}F n.m.r. spectral parameters for WF_5OMe and WF_5OPh are shown in Table 2.3,

though large solvent shifts were observed. Typical spectra are shown in Figures 2.1 and 2.2 .

TABLE 2.3

N.m.r. spectra of WF_5OMe and WF_5OPh

Compound	Solvent	δ_F (rel. CCl_3F) p.p.m.	J_{FF} Hz	J_{WF} Hz	δ_H[a] τ	J_{HF} Hz	$J_{FF}/\nu_o\delta$
WF_5OMe	C_6F_6	-118.5 (F_X) -89.5 (F_A)	66	40(F_X) 33(F_A)	4.40	1	0.040
WF_5OPh[b]	C_6F_6	-131.9 (F_X) -118.6 (F_A)	64	39(F_X)	2.50	1	0.088

[a] Mid-point of complex multiplet

[b] Values are from first-order AX_4 analysis.

The ^{19}F n.m.r. spectrum of WF_5OMe is characteristic of an AX_4 system, and that of WF_5OPh of an AB_4 system which approximates to a first-order AX_4 system. Figure 2.3 shows calculated AB_4 spectra, and the spectra of WF_5OMe and WF_5OPh match these for the appropriate values of $J_{FF}/\nu_o\delta$. The ^1H and ^{19}F signals show complex fine structure from ^1H - ^{19}F coupling.

/ Figures 2.1 - 2.3

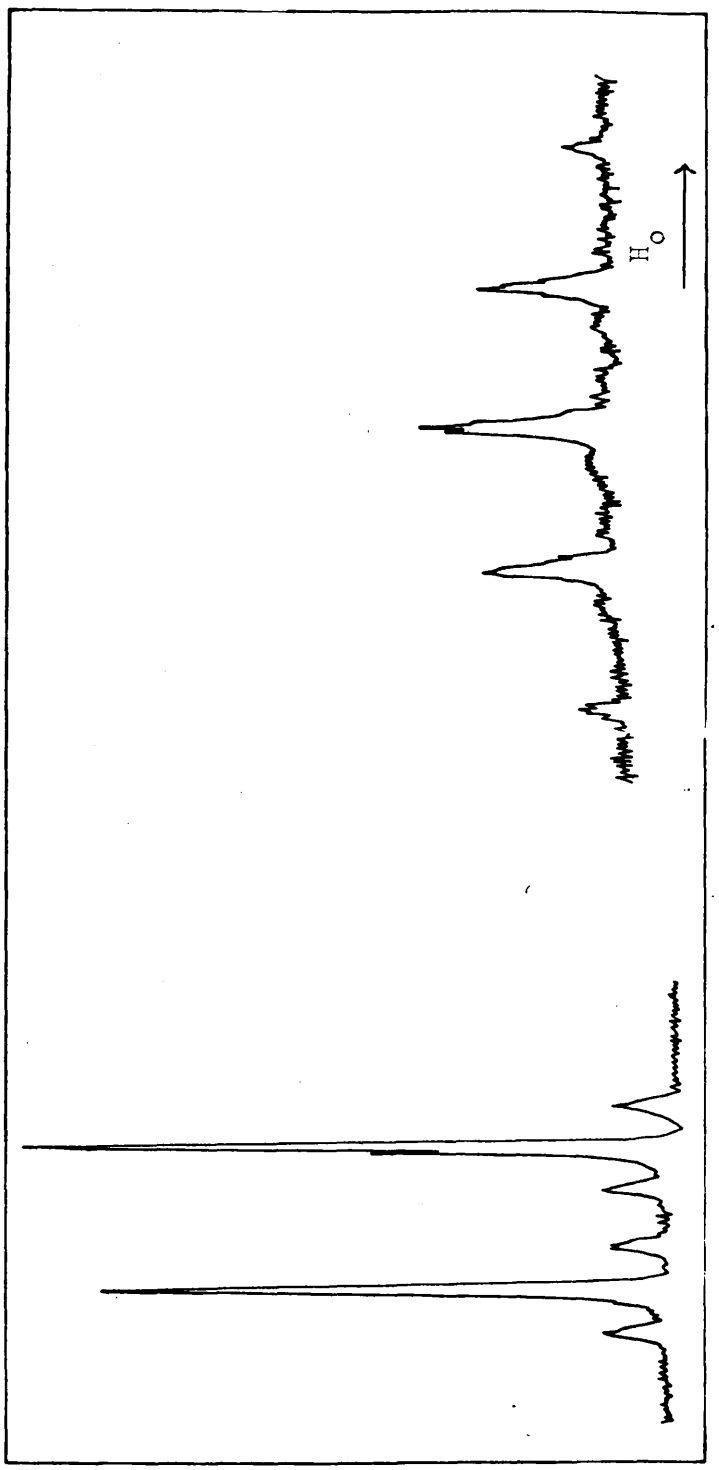


Figure 2.1: ^{19}F n.m.r. spectrum of WF_5OMe in C_6F_6
(spectral parameters are given in Table 2.3)

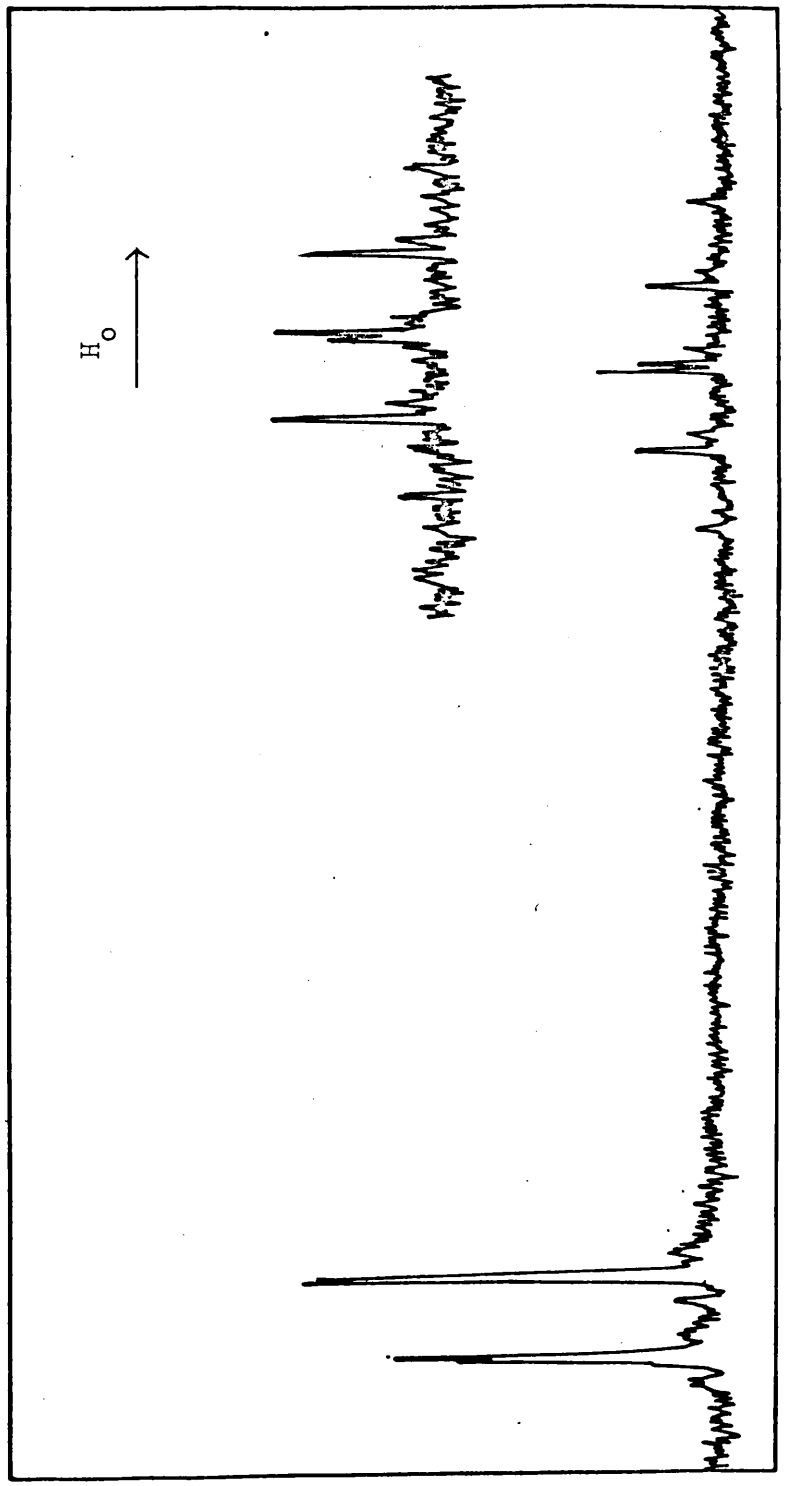


Figure 2.2: ^{19}F n.m.r. spectrum of WF_5OPh in C_6F_6
(spectral parameters are given in Table 2.3)

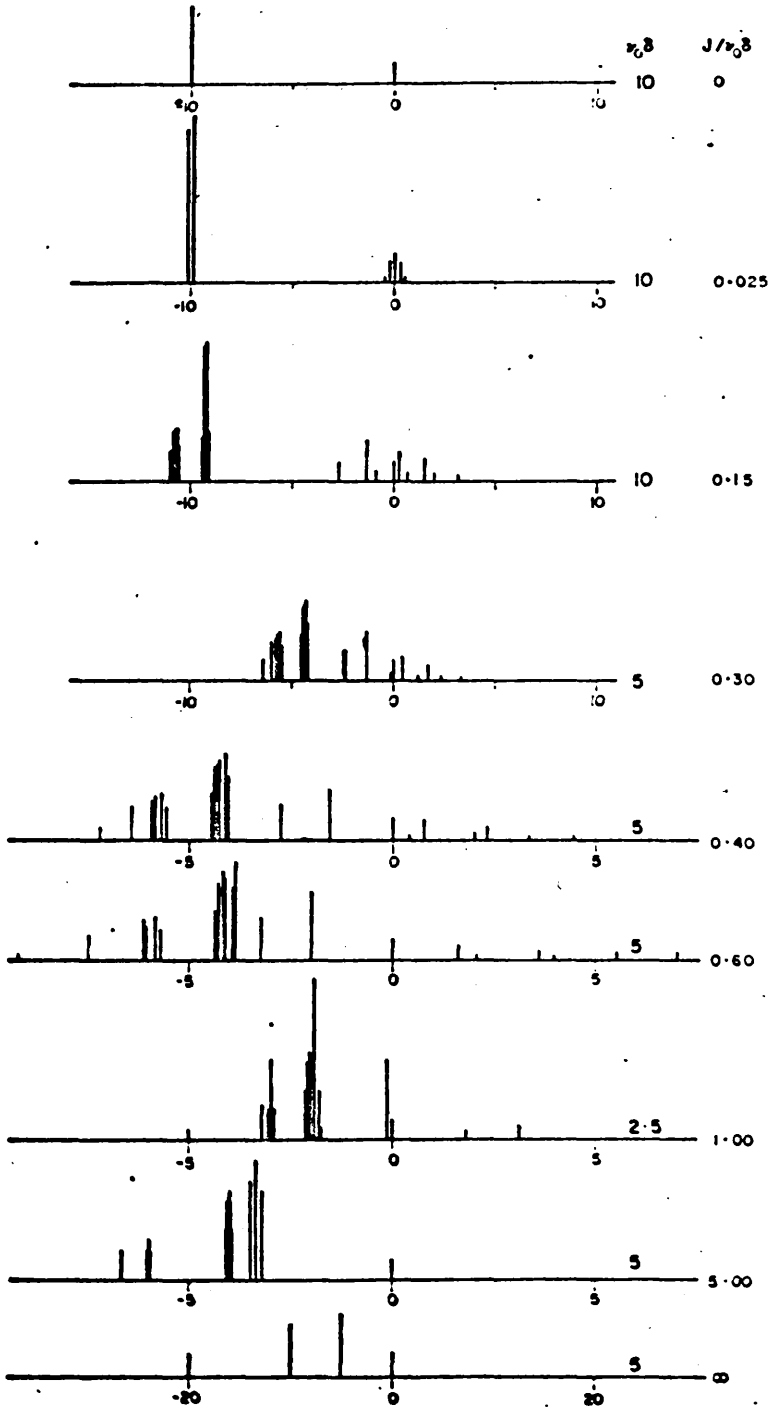
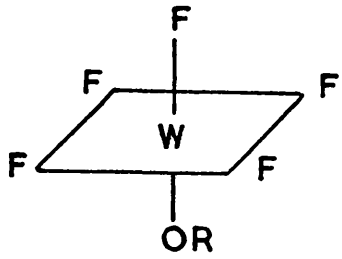


Figure 2.3: **AB_4 type theoretical spectra** [141]

The simplest interpretation of the ^{19}F n.m.r. spectra of WF_5OMe and WF_5OPh is that the compounds are monomeric in solution with an octahedral arrangement of ligands around tungsten (structure II). Because of the hygroscopic nature of these compounds it has not been possible to obtain molecular weight data. However $W(OPh)_6$ and some related chlorophenoxides of tungsten(VI) are monomeric in benzene.[153]



(II)

Assignments of the infrared spectra of WF_5OMe and WF_5OPh in the region 1000 - 400 cm^{-1} are not entirely satisfactory because of the difficulty of distinguishing the bands associated with W-O, W-F and C-O stretching frequencies (cf. refs. 11, 50, 53). The Raman spectrum of WF_5OMe in C_6F_6 is similar to that of the solid, but the solution was too dilute for definite assignments to be made.

In reactions of WF_6 with sulphite esters only one of the fluorine atoms in WF_6 is substituted for an OR group, and the reaction 2.2 does not occur.

$$WF_6 + (RO)_2SO \not\longrightarrow WF_4(OR)_2 + SOF_2 \qquad (2.2)$$

The volatile products of reactions of WF_6 with excess dimethyl and diethyl sulphites (i.e. ratio $(RO)_2SO:WF_6 \geqslant 2$) are the corresponding alkylfluorosulphite and small amounts of the corresponding alkyl fluoride. The amounts of ROS(O)F formed require the stoichiometry of equation 2.1, but WF_5OR compounds are not isolated. The amounts of unreacted $(RO)_2SO$ recovered when the ratio of reactants $(RO)_2SO:WF_6 > 2$ indicate that two moles of $(RO)_2SO$ react per mole of WF_6. The involatile products are straw-coloured liquids whose ^{19}F n.m.r. spectra indicate that at least two tungsten-fluorine compounds are present. The major signals are those characteristic of the $W_2O_2F_9^-$ ion (Table 1.3). Single resonances of much less intensity at -65 p.p.m. from CCl_3F (R = Me) and -66 p.p.m. (R = Et), with satellite peaks from $^{183}W - ^{19}F$ coupling of 69 Hz resolved only in the latter case, are also observed. Although there is considerable uncertainty in the assignment of single line n.m.r. resonances, these are assigned to WOF_4 species on the basis of the similarity of the spectral parameters to those of WOF_4 and $WOF_4.OMe_2$ (Table 1.3). The species are tentatively formulated as $WOF_4.OS(OR)_2$. The ^1H n.m.r. spectra of these products indicate that there are alkoxyl groups in at least two environments, and elemental analyses confirm the presence of carbon, hydrogen, fluorine, sulphur and tungsten.

Similar products are obtained from the reaction of WF_5OMe with dimethyl sulphite. WF_5OMe dissolves slowly in $(MeO)_2SO$ yielding

a colourless solution. The ^{19}F and ^{1}H n.m.r. spectra of this solution after 30 minutes and after 12 days are shown in Figures 2.4 and 2.5. Signals A and J are characteristic of WF_5OMe (cf. Table 2.3), the signal from the axial fluorine being too weak for detection. Signals C, F and K are characteristic of cis $WF_4(OMe)_2$ (Table 3.2) and E and G of MeOS(O)F(Table 2.2); H, L and L′ are characteristic of methyl fluoride,[154] although the latter signal is partially obscured by the doublet O of MeOS(O)F. The major ^{19}F signals B and D show satellite peaks from $^{183}W - ^{19}F$ coupling, and arise from tungsten-fluorine species. The doublet D and the multiplet G have the same coupling constant of 59 Hz, and are characteristic of the $W_2O_2F_9^-$ ion (Table 1.3; the parameters for the singlet B (δ_F rel. CCl_3F = -66 p.p.m., J_{WF} = 68 Hz) are similar to those of WOF_4 and $WOF_4.OMe_2$ (Table 1.3), the chemical shift being close to those assigned to $WOF_4.OS(CR)_2$ species above. Further support for the assignment of B to a WOF_4 species comes from ^{183}W n.m.r. measurements (chapter 4). The singlet P at 6.41τ in the ^{1}H n.m.r. spectra has the same chemical shift as $(MeO)_2SO$,[155] and is assigned to both bulk and coordinated $(MeO)_2SO$.

The ^{19}F n.m.r. spectrum recorded after 12 days shows a substantial increase in the intensity of the signals of the $W_2O_2F_9^-$ ion. The absence of signals characteristic of WF_5OMe indicates that the reaction has gone to completion. The ^{1}H n.m.r. spectrum after 12 days shows

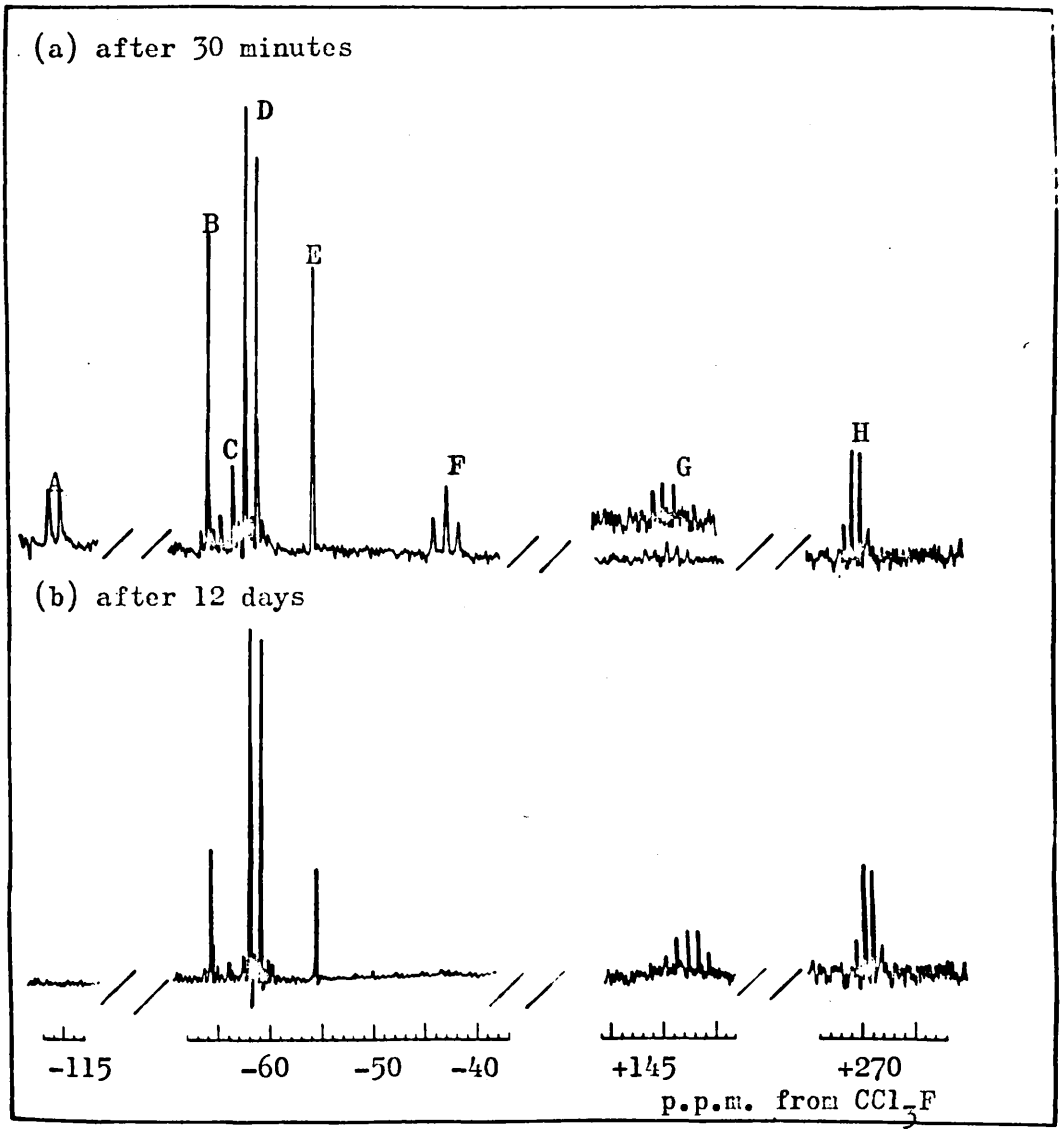


Figure 2.4: ^{19}F n.m.r. spectra of WF_5OMe in $(MeO)_2SO$

(spectral parameters are given in the experimental section)

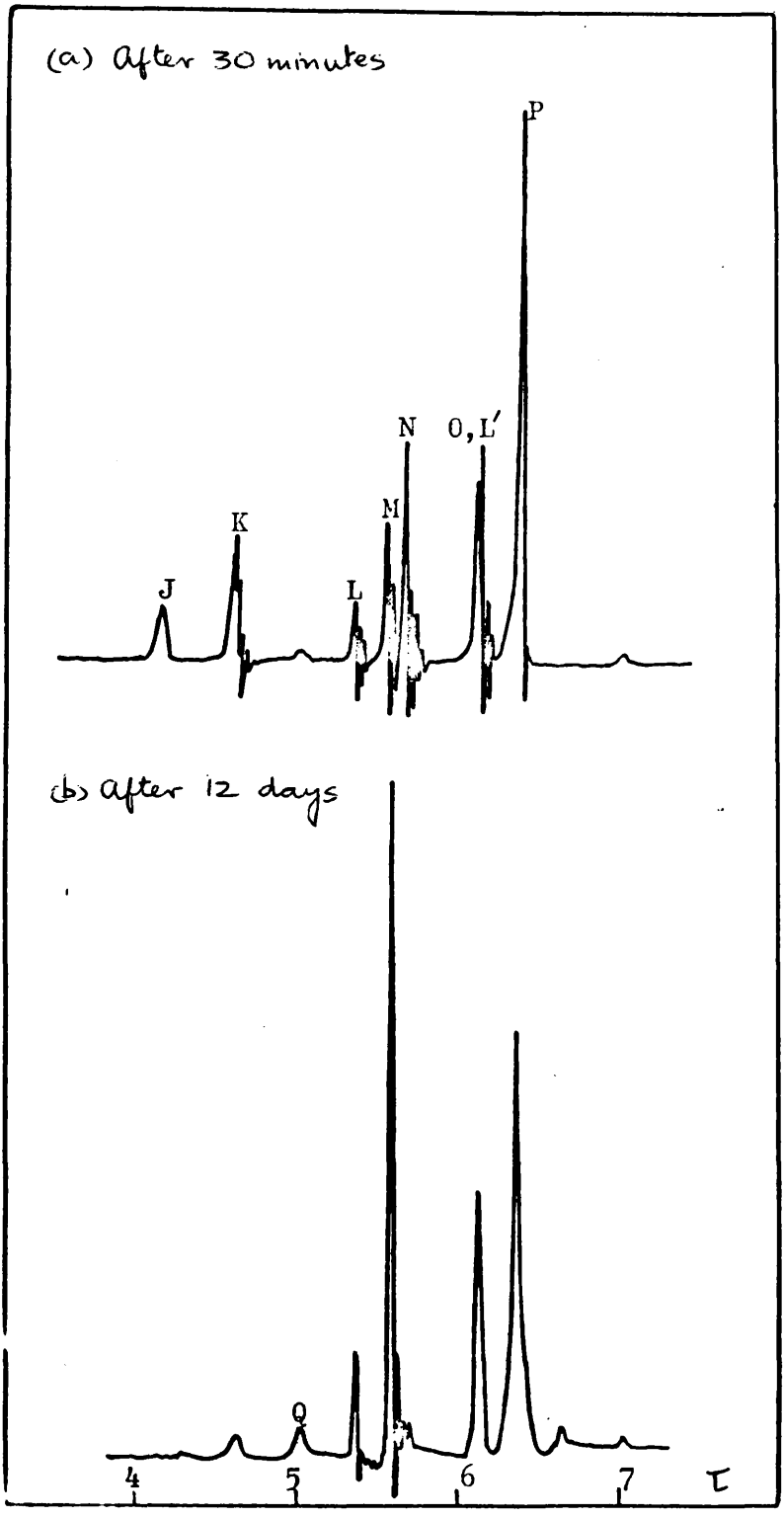


Figure 2.5: ^{1}H n.m.r. spectra of WF_5OMe in $(MeO)_2SO$

(spectral parameters are given in the experimental section)

an intense signal at 5.62τ which does not exactly coincide with either M or N, but is assigned as N. It is possible that this signal arises from the cation associated with the $W_2O_2F_9^-$ anion, and it is tentatively formulated as the trimethoxysulphonium cation, $(MeO)_3S^+$. The disappearance of signal M is not understood.

The reaction of WF_5OMe with $(MeO)_2SO$ is consistent with equations 2.3 - 2.6:

$$WF_5OMe + (MeO)_2SO \longrightarrow (MeO)_3S^+WOF_5^- \quad (2.3)$$

$$WF_5OMe + (MeO)_2SO \longrightarrow WOF_4.OS(OMe)_2 + MeF \quad (2.4)$$

$$WOF_4.OS(OMe)_2 + (MeO)_3S^+WOF_5^- \longrightarrow (MeO)_3S^+ W_2O_2F_9^- + (MeO)_2SO \quad (2.5)$$

$$WF_5OMe + (MeO)_2SO \longrightarrow WF_4(OMe)_2 + MeOS(O)F \quad (2.6)$$

These reactions, and the analagous reactions for WF_5OEt, also account for the products obtained from the reactions of WF_6 with excess dimethyl and diethyl sulphites.

The disappearance after 12 days of the signals characteristic of $WF_4(OMe)_2$ suggests that the further reaction 2.7 may occur.

$$WF_4(OMe)_2 + (MeO)_2SO \longrightarrow WF_{6-n}(OMe)_n \ (n \geq 3) + MeOS(O)F \quad (2.7)$$

The weak ^1H n.m.r. signal Q is not inconsistent with the species $WF_{6-n}(OMe)_n$, $n \geq 3$. (Table 3.2). There is, however, no significant increase in the intensity of the signals E and O from MeOS(O)F.

The Reaction of Tungsten Hexafluoride with Sulphur Trioxide

Pyrosulphuryl fluoride, $S_2O_5F_2$, is formed in the reaction of WF_6 with sulphur trioxide, and a reaction similar to that between VF_5 and sulphur trioxide[114] may be visualised:

$$WF_6 + SO_3 \longrightarrow WF_{6-n}(SO_3F)_n \longrightarrow WOF_4 + S_2O_5F_2 \qquad (2.8)$$

The ^{19}F n.m.r. spectra of the tungsten-containing products are complex, and it is not possible to make definite assignments of the peaks. The complexity of these spectra may arise from exchange processes, second-order splittings for $WF_{6-n}(SO_3F)_n$ compounds, or the presence of polymeric species. In the absence of information about the nature of the tungsten-containing products the origin of $S_2O_5F_2$ cannot be stated with certainty.

The Reactions of Tungsten Hexafluoride with some Phosphorus Esters

This section describes the reactions of WF_6 with trimethyl phosphite, dimethyl phosphite and dimethyl methylphosphonate, and of WF_5OMe with trimethyl phosphite. The products from these reactions are summarised in Table 2.4, and Table 2.5 summarises the ^1H and ^{19}F n.m.r. spectral data for some of the products and analogous compounds.

TABLE 2.4

Reactants (mmoles)	Reaction Conditions	Products
WF_6 (2.4) $P(OMe)_3$ (2.1)	0^o, ½ hr.	WF_5OMe; $WOF_4.OP(F)(OMe)Me$ (?); MeF; + invol. white solid.
WF_6 (4.5) $P(OMe)_3$ (15)	$<0^o$, 12 hr.	$(MeO)_2PF$; $(MeO)_2P(O)Me$; $MeP(O)(F)OMe$; $WOF_4.OP(OMe)_2Me$; $(MeO)_3PMe^+ WOF_5^-$; + unreacted $P(OMe)_3$
WF_6 (3.7) $(MeO)_2P(O)Me$ (6.5)	25^o, ½ hr.	$MeP(O)(F)OMe$; WF_5OMe; $WOF_4.OP(OMe)_2Me$; MeF
WF_5OMe (1.1) $P(OMe)_3$ (1.5)	0^o, ½ hr.	$(MeO)_2P(O)Me$; $WOF_4.OP(OMe)_2Me$; $(MeO)_3PMe^+ WOF_5^-$

WF_6 reacts vigorously with trimethyl phosphite above 0^o, and explosions may occur if equimolar quantities of reactants are used. Reactions with an excess of trimethyl phosphite are more moderate. The compounds are miscible at -80^o, forming an intensely yellow solution, which, on warming slowly to 0^o, yields a deep-orange oil. This decomposes rapidly above 0^o to yield a variety of products, which depend on the stoichiometry and the conditions of the reaction.

TABLE 2.5

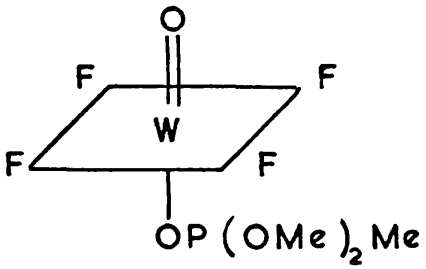
Compound	Solvent	δ_H (OMe) τ	$\delta_{H(Me)}$ τ	δ_F p.p.m. (rel. CCl_3F)	J_{PH} (OMe) Hz	J_{PH} (Me) Hz	J_{FF} Hz	J_{WF} Hz	J_{PF} Hz	J_{HF} Hz	Ref.
$P(OMe)_3$		6.28			10.7						156
$PF(OMe)_2$		6.41		+63.1	10.1				1208	0.6	137
$MeP(O)(F)OMe$				+62					1039	6.0 (FPCH)	137
$(MeO)_2P(O)Me$	neat	6.34	8.57		11.0	17.3					157
$WOF_4.OP(OMe)_2Me$	neat	6.09	8.23	-60.1	12	18		70	1.7		109
$(MeO)_3PMe^+WOF_5^-$	CD_3CN	5.92	7.89	-49.8 (F_X) +84.2 (F_A)	11	17	53	72(F_X)			
$(MeO)_3PMe^+PF_6^-$	$(CD_3)_2CO$	5.7	7.6	+73	11	18			707		137
$^nPrN_4^+WOF_5^-$	CH_3CN			-49.4 (F_X) +82.8 (F_A)			53	70(F_X)			35
CH_3F			5.90	+271.9						46.4	154

A reasonably pure sample of trimethoxymethyl oxopentafluorotungstate(VI), $(MeO)_3PMe^+ WOF_5^-$, a white solid, can be obtained from the reaction of WF_5OMe with $P(OMe)_3$ if the temperature is carefully controlled. The ^1H n.m.r. spectral parameters are very similar to those of $(MeO)_3PMe^+ PF_6^-$ [137] and the ^{19}F n.m.r. spectral parameters are almost identical to those of the WOF_5^- ion.[35]

It has been observed[109] that $(MeO)_3PMe^+ WOF_5^-$ in the mixture of involatile products from the reaction of WF_6 with excess $P(OMe)_3$ decomposes at 90° to yield an analytically pure sample of oxotetrafluoro(dimethyl methylphosphonate)tungsten(VI), $WOF_4.OP(OMe)_2Me$ and methyl fluoride (2.9).

$$(MeO)_3PMe^+ WOF_5^- \longrightarrow WOF_4.OP(OMe)_2Me + MeF \qquad (2.9)$$

$WOF_4.OP(OMe)_2Me$ is a colourless liquid which can be distilled very slowly at 25° in vacuo. The ^1H n.m.r. signals show small downfield shifts from uncomplexed $(MeO)_2P(O)Me$, and there is good agreement between the $^1H - ^{31}P$ coupling constants. The ^{19}F n.m.r. spectrum consists of a main doublet from $^{19}F - ^{31}P$ coupling, and doublet sidebands from $^{19}F - ^{183}W$ coupling. The spectral parameters are similar to those of WOF_4 and $WOF_4.OMe_2$ (Table 1.3). The inherent ambiguity of n.m.r. spectroscopic equivalence of ^{19}F nuclei precludes a definite assignment of the structure of this complex. If monomeric, an octahedral structure with the dimethyl methylphosphonate ligand in a site trans to the terminal oxygen is required (III).



(III)

The alternative structure is a polymer with a coordination number for tungsten of greater than six, in which n.m.r. spectroscopic equivalence of the ^{19}F nuclei results from a fast exchange process in which the $>WF_4OP(OMe)_2Me$ bond arrangement is preserved. The magnitude of the ^{31}P - ^{19}F coupling constant (1.7 Hz) suggests that dimethyl methylphosphonate coordinates via oxygen rather than phosphorus, as P - F coupling over 1 or 2 bonds gives much larger values of J_{PF} (cf. $WF_6.PMe_3$, J_{PF} = 73 Hz[35]). Crystal structure determinations show that oxygen is the donor atom in $SbCl_5.Me_3PO$, $SbCl_5.POCl_3$, $NbCl_5.POCl_3$ and $TaCl_5.POCl_3$.[115].

A reaction scheme can be devised to account for the observed products. An initial reaction involving substituent exchange between

WF_6 and $P(OMe)_3$ provides a route to dimethyl fluorophosphite and pentafluoromethoxotungsten(VI):

$$P(OMe)_3 + WF_6 \longrightarrow PF(OMe)_2 + WF_5OMe \qquad (2.10)$$

With equimolar quantities of reactants the yield of WF_5OMe is not quantitative, and $PF(OMe)_2$ is not isolated. With an excess of $P(OMe)_3$, $PF(OMe)_2$ is isolated, but WF_5OMe is not. In both cases there is no evidence for the formation of methyl difluorophosphite, PF_2OMe, or phosphorus trifluoride.

The further reaction of WF_5OMe can be explained in terms of its participation in the Michaelis-Arbusov[138] rearrangement of trimethyl phosphite (2.11).

$$P(OMe)_3 + RX \rightleftharpoons [(MeO)_3PMe^+ X^-] \longrightarrow RP(O)(OMe)_2 + MeX \,. \qquad (2.11)$$

The Michaelis-Arbusov rearrangement occurs in the presence of not only simple alkyl halides, but also organic polyhalides such as methylene bromide or carbon tetrachloride, haloethers, haloketones, and halocarboxylic acids and their derivatives. The phosphonium intermediate has been isolated in the reaction between triphenyl phosphite and methyl iodide.[158] $(MeO)_3PMe^+WOF_5^-$ is the intermediate required in 2.11 if RX = WF_5OMe, and since R = Me, the reaction is a true isomerization (2.12).

$$P(OMe)_3 + WF_5OMe \rightarrow (MeO)_3PMe^+WOF_5^- \longrightarrow (MeO)_2P(O)Me + WF_5OMe \,. \qquad (2.12)$$

Direct confirmation for the first stage of 2.12 comes from the reaction of WF_5OMe with $P(OMe)_3$ (Table 2.4) which gives $(MeO)_3PMe^+WOF_5^-$ in high yield. A similar Michaelis-Arbusov intermediate, $(MeO)_3PMe^+PF_6^-$, has been isolated from the reaction of PF_5 with $P(OMe)_3$.[137] The second stage of 2.12 (i.e. the rearrangement of $(MeO)_3PMe^+WOF_5^-$ to yield $(MeO)_2P(O)Me$) is slower than for $(MeO)_3PMe^+PF_6^-$,[159] and in one reaction unreacted $P(OMe)_3$ was recovered. The products of the decomposition of $(MeO)_3PMe^+WOF_5^-$ at 90° and at ambient temperatures (the latter, in CD_3CN solution and followed by ^{19}F n.m.r. spectroscopy, requires several months for completion) are $WOF_4.OP(OMe)_2Me$ and MeF. There is, therefore, no direct evidence that WF_5OMe is regenerated as required by the second stage of 2.12. $WOF_4.OP(OMe)_2Me$ may be formed either by the decomposition of regenerated WF_5OMe in the presence of $(MeO)_2P(O)Me$ (cf. 2.14 below), or directly from the decomposition of $(MeO)_3PMe^+WOF_5^-$.

The products of the reaction of WF_6 with dimethyl methylphosphonate at 25° were identified by ^1H and ^{19}F n.m.r. spectroscopy, and the reaction is consistent with:

$$(MeO)_2P(O)Me + WF_6 \longrightarrow MeP(O)(F)OMe + WF_5OMe \qquad (2.13)$$

$$(MeO)_2P(O)Me + WF_5OMe \rightarrow WOF_4.OP(OMe)_2Me + MeF \ . \qquad (2.14)$$

It is likely that the origin of methyl methylphosphonofluoridate, $MeP(O)(F)OMe$, in the reactions of WF_6 with $P(OMe)_3$ is in the process

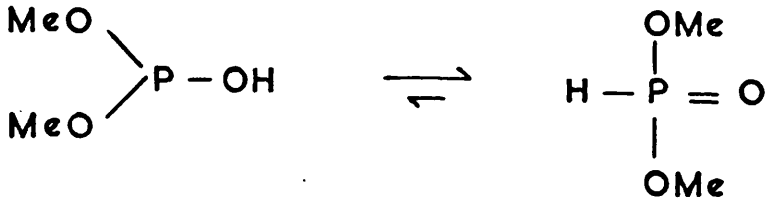
2.13. It has been suggested[137] that $PF(OMe)_2$ might undergo a Michaelis-Arbusov rearrangement to yield MeP(O)(F)OMe:

$$PF(OMe)_2 \longrightarrow MeP(O)(F)OMe \qquad (2.15)$$

Such a process could also explain the formation of MeP(O)(F)OMe in the reactions of WF_6 and $P(OMe)_3$.

In some of the reactions described above there were small amounts of unidentified volatile products, and it is likely that other complex side-reactions are involved.

The major product of the reaction of WF_6 with dimethyl phosphite is phosphorus trifluoride. SiF_4 is produced, and extensive hydrolysis occurs, suggesting that HF is a reaction product. In general a hydroxyl group bonded to trivalent phosphorus is unstable with respect to the pentavalent phosphorus compound containing a phosphoryl group:[160]



(IV) (V)

Substituent exchange between WF_6 and IV would yield PF_3, and IV would be generated from V as the reaction proceeded. The other product then is formally $WF_3(OMe)_2OH$, and the F—W—OH system is likely to be unstable with respect to W=O and HF.

Reactions of Methoxy and Phenoxy Tungsten(VI) Pentafluorides

The reactions of WF_5OMe ~~and WF_5OPh~~ with dialkyl sulphites and trimethyl phosphite have been described above.

WF_5OMe and WF_5OPh form adducts with nitrogen bases, but these have not been characterised. A dark brown solid which analyses as WF_5OMe,1.3py results from the reaction of WF_5OMe with pyridine, but the present work has not distinguished between its formulation as an adduct of WF_5OMe or the methylpyridinium salt, $pyMe^+WOF_5^-$. Trimethylamine and WF_5OPh react to form a red involatile solid which was not investigated in detail, but was used to remove small amounts of WF_5OPh from $PhOS(O)F$.

Acetonitrile is not a suitable solvent for WF_5OMe as a vigorous reaction occurs, yielding a bright yellow solution whose F^{19} n.m.r. spectrum indicates the presence of WOF_5^- and $W_2O_2F_9^-$. A slow reaction also occurs between WF_5OMe and benzene, and a small quantity of toluene is formed, consistent with:

$$C_6H_6 + WF_5OMe \longrightarrow C_6H_5Me + WOF_4 + HF . \qquad (2.16)$$

However, as HF is produced extensive hydrolysis occurs, and, while tungsten-fluorine compounds are present in the reaction mixture, a pure sample of WOF_4 is not obtained.

It was thought that reaction of WF_5OMe with dialkyl ethers would provide a convenient route to WOF_4 — ether complexes according to:

$$WF_5OMe + R_2O \longrightarrow WOF_4.OR_2 + MeF \qquad (2.17)$$

WF_5OMe reacts with dimethyl ether at 135° with evolution of methyl fluoride, but the reaction is not a convenient route to $WOF_4.OMe_2$, a brown oil being obtained. With diethyl ether reaction occurs at 20° to yield methyl fluoride and an involatile liquid which solidifies after several hours. The major signals in the ^{19}F n.m.r. spectrum of this liquid are those characteristic of the $W_2O_2F_9^-$ ion (Table 1.3), and a weak singlet at -65.5 p.p.m. from CCl_3F is consistent with the presence of the species $WOF_4.OEt_2$ (cf. data for $WOF_4.OMe_2$ in Table 1.3). Some evidence for the formation of $WOF_4.OEt_2$ in the reaction of WF_6 with diethyl ether has already been obtained (chapter 1).

The data for the reaction of WF_5OMe with diethyl ether are not inconsistent with the initial formation of WOF_5^- and $WOF_4.OEt_2$,

$$WF_5OMe + Et_2O \longrightarrow X^+WOF_5^- \quad (X = Et_2OMe^+ \ ?) \qquad (2.18)$$

$$WF_5OMe + Et_2O \longrightarrow WOF_4.OEt_2 + MeF \ , \qquad (2.19)$$

followed by the further slower reaction:

$$WOF_4.OEt_2 + WOF_5^- \longrightarrow W_2O_2F_9^- + Et_2O \quad . \qquad (2.20)$$

Discussion of the Reactions

The reactions of WF_6 with dimethyl sulphoxide, sulphite esters, phosphite esters and dimethyl methylphosphonate probably proceed via the initial formation of a donor-acceptor complex, similar to those of WF_6 with other donor molecules in which the coordination number of tungsten is greater than six (chapter 1). The WF_6 - DMSO adduct may undergo an oxygen abstraction reaction yielding tungsten oxotetrafluoride:

$$WF_6 + OSMe_2 \longrightarrow WOF_4 + F_2SMe_2 \quad . \qquad (2.21)$$

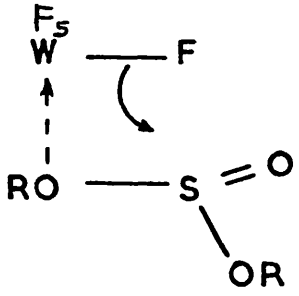
Me_2SBr_2 is stable, but Me_2SCl_2 decomposes to CH_2ClSMe and HCl.[132] Me_2SF_2 is unstable,[161] and the expected decomposition products are CH_2FSMe and HF:

$$Me_2SF_2 \longrightarrow CH_2FSMe + HF \quad . \qquad (2.22)$$

The analogous compound Me_2SeF_2 is, however, stable.[162] α-Fluorosulphides are unstable at ambient temperatures,[163] and further decomposition of CH_2FSMe might occur, with evolution of HF. The origin of CH_2FOCH_2F is not clear, and, as HF is formed, other reactions in addition to those described may occur. CH_2FOCH_2F could result from a reaction involving attack on the glass. WOF_5^- and WOF_4 are hydrolysis products of WF_6 and its derivatives (chapter 1), and it is thought that these

react to yield $W_2O_2F_9^-$ (cf. equation 1.5) which is a major product in the reaction of WF_6 with DMSO.

The exchange reaction between WF_6 and sulphite esters can be visualised as proceeding via a weak donor-acceptor complex (VI) in which the oxygen of an OR group is bonded to the tungsten atom of WF_6. Similar intermediates can be invoked for the reactions of WF_6



(VI)

with phosphite esters and dimethyl methylphosphonate.

Part of the energy change in a substituent-exchange reaction of WF_6 arises from the difference in the bond energy terms for

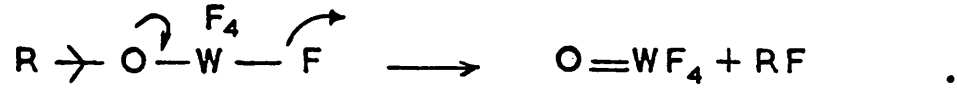
$$W—F + X—OR \longrightarrow W—OR + XF \quad , \quad (X = S, P)$$

and a large difference in the sum of the bond energy terms of the products and the reactants will favour the reaction. The average

P — F and P — O bond energies in PF_3 and $P(OMe)_3$ are ~~91~~ 117 and ~~117~~ 91 kcal/mole respectively.[166] The average bond energies of $WO_{3(g)}$ and $WF_{6(g)}$ are 151 and 122 kcal/mole respectively,[165] giving some indication that the difference in W — OR and W — F bond energy terms will favour the reaction.

$p\pi$-$d\pi$ Bonding in RO — S bonds is greater in sulphur(VI) than in sulphur(IV) esters, and is increased by the presence of electronegative substituents.[168] This may account for the lack of reaction between WF_6 and dimethyl sulphate[108] and alkylfluorosulphites. It is thought that WF_6 fluorinates the S=O bond in DMSO (2.21), but it does not fluorinate the S=O bond in sulphite esters and dimethyl sulphone consistent with the higher bond orders of the latter.

The thermal stabilities of WF_5OR compounds are in the order Ph>Me>Et, and are intermediate between methoxofluorides of non-metals, e.g. PF_4OMe,[169] and the polymeric ethoxofluorides of titanium,[170] niobium and tantalum.[171] The order of thermal stabilities can be related to the inductive properties of R. The electron releasing methyl and ethyl groups will increase the tendency towards the formation of a tungsten-oxygen multiple bond:



This process need not be intramolecular. The electron

withdrawing phenyl group on the other hand will stabilise the R — O — W bond system.

The thermal decomposition of WF_5OMe at 135° affords a convenient route to tungsten oxotetrafluoride, WOF_4, in high yield (>75%). WOF_4 has been prepared by the action of anhydrous hydrogen fluoride on $WOCl_4$,[24] by the action of an oxygen-fluorine mixture on tungsten metal at elevated temperatures,[172] by the action of dichlorodifluoromethane on WO_2 at 525°,[173] and by the reaction of WF_6 with WO_3 at 400°.[35] It has also been obtained from a fused mixture of an alkali metal halide and WO_3.[49]

WF_5OMe and WF_5OPh, like WF_6 behave as Lewis acids, and the yellow colours of solutions of WF_5OMe in C_6H_6 and C_6F_6 probably arise from intermolecular "charge-transfer" interaction similar to that observed between WF_6 and organic donor solvents (chapter 1). McLean[82] has recorded the u.v.-visible spectra of WF_5OMe and WF_5OPh in several donor solvents, and found solvent dependence of the spectra only for WF_5OMe. Intramolecular "charge-transfer" between the π-system of the phenyl group and the vacant 5d orbitals of the tungsten atom probably accounts for the colour of WF_5OPh and its solutions.

WF_5OMe is an interesting molecule. Its chemical reactivity is associated with its ability to lose a methyl group either as Me^+ (which combines with a suitable substrate) to yield WOF_5^-, or MeF to yield WOF_4. It is potentially useful for the preparation of other oxofluoro-

derivatives of tungsten and the methylation of unsaturated organic molecules. Neither of these possibilities was systematically examined, and they provide scope for future work.

Conclusions

The reactions of WF_6 with sulphite esters, phosphite esters and dimethyl methylphosphonate involve the exchange of F and OR substituents, and further reaction of the WF_5OR species formed (R = Me, Et) occurs in some cases. The thermal stabilities of WF_5OR compounds are in the order Ph > Me > Et. The reactions of WF_5OMe are consistent with its ability to lose Me^+ yielding WOF_5^- or MeF yielding WOF_4.

The reaction of WF_6 with dimethyl sulphoxide is complicated by the formation of HF and may involve the fluorination of the sulphur-oxygen bond. One of the products of the reaction is formulated as bis(monofluoromethyl)ether, CH_2FOCH_2F. Pyrosulphuryl fluoride, $S_2O_5F_2$, is formed in the reaction of WF_6 with sulphur trioxide, but its origin cannot be stated with certainty as the nature of the tungsten-containing products has not been elucidated.

EXPERIMENTAL SECTION

Chemicals

WF_6 was purified as described previously (chapter 1), and where necessary, reactants and solvents were purified by literature methods.[100] Dimethyl sulphoxide (B.D.H., spectroscopic grade) was refluxed for several hours over CaH_2, and fractionally distilled under vacuum before use. Dimethyl sulphite, diethyl sulphite, dimethyl methylphosphonate (Aldrich), dimethyl phosphite (Emanuel) and pyridine (B.D.H., anhydrous grade) were degassed, stored over activated Linde 4A molecular sieves, and vacuum distilled before use. Diphenyl sulphite was prepared from PhOH and $SOCl_2$,[174] and stored over activated molecular sieves. Trimethyl phosphite (B.D.H.) and hexafluorobenzene (Imperial Smelting Co.) were degassed, stored over sodium wire, and vacuum distilled before use. Sulphur trioxide (Hardman and Holden) was vacuum distilled and used without further purification, and dimethyl sulphone (Emanuel) was degassed (10^{-4} mm) for several hours before use. Trimethylamine was vacuum distilled twice through -78°. Benzene, deuteroacetonitrile, dimethyl ether and diethyl ether were dried as described previously (chapter 1).

Experimental procedure

The reactions were performed in a high vacuum system; glass reaction vessels fitted with teflon stopcocks and stainless-steel

or monel-metal bombs fitted with Hoke valves were used as appropriate (see Appendix). Rigorous precautions were taken to exclude trace amounts of moisture. WF_6 and volatile reactants were condensed together into the reaction vessels, which were cooled with liquid nitrogen, and the mixture was allowed to warm slowly until reaction occurred. Dimethyl sulphoxide was distilled directly (30°, 10^{-2} mm) into a reaction flask. Diphenyl sulphite, dimethyl sulphone and involatile reaction products were handled in a dry-box. WF_5OPh, and in some cases WF_5OMe, were prepared in situ by reaction of WF_6 with the appropriate sulphite ester.

The reactions of WF_6 and WF_5OMe with the phosphorus esters were complex, and yielded mixtures of products which could not be easily separated. The high toxicity[137] of some of these products made it desirable to contain them within closed systems, and, since most were known compounds, identification by comparison of their ^1H and ^{19}F n.m.r. spectral parameters with those of authentic samples (Table 2.5) was generally satisfactory. One limitation of this method is that products present in trace amounts are not detected. All the n.m.r. spectra gave first-order patterns, with signals in the correct intensity ratios. Small discrepancies, particularly in chemical shifts, between published and observed values were presumed to arise from solvent effects and/or small errors in referencing techniques. ^{19}F n.m.r. spectra were not always recorded on maximum

scale expansion, and smaller splittings were not always resolved. In some cases the compositions of mixtures were estimated (± 5%) from the intensity of n.m.r. signals.

Reactions of Tungsten Hexafluoride

(1) Tungsten hexafluoride and dimethyl sulphoxide

Several reactions were carried out with the mole ratio of reactants DMSO:WF_6 varied from 1:1 to 4:1, and the products were similar in each case. Unreacted WF_6 was recovered only with DMSO:WF_6 <1, and with DMSO:WF_6 ⩾ 2 significant quantities of volatile products were obtained.

(a) WF_6 (6.0 g, 20 mmoles) and DMSO (1.3 g, 17 mmoles) gave a transient yellow colour at 0°, followed by a vigorous exothermic reaction. After 30 minutes the temperature was raised to 20°, and a pale yellow viscous liquid was obtained. There was considerable etching of the glass reaction vessel.

The fraction volatile at -78° was a mixture of WF_6 and SiF_4 (identified by i.r.[101, 103]).

Elemental analysis of the involatile product gave: C, 6.85; H, 1.79; S, 9.22; F, 16.3; W, 49.3% (atomic ratio, F:W = 3.2:1). Infrared spectrum (liquid film, 4000 - 400 cm^{-1}) : 3016s, 2935s, 1425s, 1335m, 1319sh, 1164sh, 1153m, 1068sh, 1045sh, 1022sbr, 988br, 945s, 874m, 756m, 702s, 670-625sbr cm^{-1}.

The ^{19}F n.m.r. spectrum of the involatile product in CD_3CN (CCl_3F ref.) consisted of a major signal at -62.6 p.p.m. (doublet, J_{FF} = 58 Hz, J_{WF} = 71 Hz), and signals of less intensity at - 144.2 p.p.m. (singlet, J_{WF}, partially resolved, = 40 Hz), -52.1 p.p.m. (doublet, J_{FF} = 49 Hz), +144.8 p.p.m. (multiplet, minimum of 7 lines, J_{FF} = 58 Hz, J_{WF} = 50 Hz) and +147.2 p.p.m. (multiplet, minimum of 3 lines, J = 50 Hz). Some of the peaks of the latter two multiplets overlapped. The ^1H n.m.r. spectrum consisted of major singlets at 6.90τ and 7.19τ, and minor singlets at 6.67τ and 7.65τ. With the exception of the last value, these are all to low field of DMSO (7.57τ[175]). On the basis of the similarity of the ^{19}F n.m.r. spectral parameters to those in Tables 1.3 and 1.5, a partial assignment was made (Table 2.6).

TABLE 2.6

Product	δ_F, p.p.m. (rel. CCl_3F)	J_{FF} Hz	J_{WF} Hz
$WF_6.OSMe_2$	-144.2		40
$W_2O_2F_9^-$	-62.6 (F_X)	58	71
	+144.8 (F_A)	58	50
WOF_5^-	-52.1[a] (F_X)	49	
	- (F_A)		

[a] Weak signal, F_A not observed.

(b) WF_6 (38.8 g, 130 mmoles) and DMSO (23.3 g, 298 mmoles) reacted at 0° yielding, in addition to products similar to those described above, a liquid volatile at 0° (1.0 g) which slowly attacked glass depositing white solids. This product was examined as follows: Mass spectrum (source 200°, el. beam 70 eV, prominent peaks only with relative intensities in brackets): m/e, 111(3); 98(1); 94(2); 93(1); 89(1); 85(3); 83(2); 82(2); 81(35); 79(1); 75(1); 64(4); 63(15); 62(2); 61(4); 60(4); 53(10); 49(3); 47(2); 46(1); 45(3); 35(2); 34(2); 33(100); 32(4); 31(18); 30(7); 29(43).

Some of the ions were identified by mass measurement (Table 2.7).

TABLE 2.7

m/e	Ion	Mass	Theory
111	?	111.02571	
81	$C_2H_3F_2O^+$	81.01514	81.01518
63	$C_2H_4OF^+$	63.02427	63.02460
33	CH_2F^+	33.01398	33.01404
31	CH_3O^+	31.01833	31.01838

Infrared spectrum (vapour phase, 10 mm, 4000 - 400 cm^{-1}) : 3021sh, 3010m, 2982w, 2964m, 2938m, 2924sh, 2917m, 2860w, 1850w, 1837w, 1820w,

1747w, 1444w, 1438w, 1430w, 1310w, 1275w, 1268w, 1260w, 1192s, 1184s, 1102-1070wbr, 1013s, 1005s, 997s cm^{-1}.

The ^{19}F n.m.r. spectrum (neat liquid, CCl_3F ref.) consisted of a multiplet at +156.6 p.p.m. (minimum of 9 lines, separations 55 and 6 Hz, see Figure 2.6). The ^{1}H n.m.r. spectrum consisted of two identical multiplets at 4.42τ and 5.34τ each with a minimum of 4 lines (see Figure 2.7). In some samples a singlet was observed at 7.98τ, which may have arisen from Me_2S (7.92τ[155]). The ^{1}H n.m.r. spectrum was analysed by the method of Harris[140] for an $X_2AA'X_2'$ system (X = H, A = F) where $J_{XX'} = 0$, and the following coupling constants were obtained: $J_{HF} = 54$, $J_{HF'} = 0.8$, $J_{FF'} = 11$ Hz.

(2) Tungsten hexafluoride and dimethyl sulphite

Several ratios of reactants were used to establish the stoichiometry of the reactions of WF_6 with sulphite esters and these are summarised in Table 2.8

/ Figures 2.6, 2.7
Table 2.8

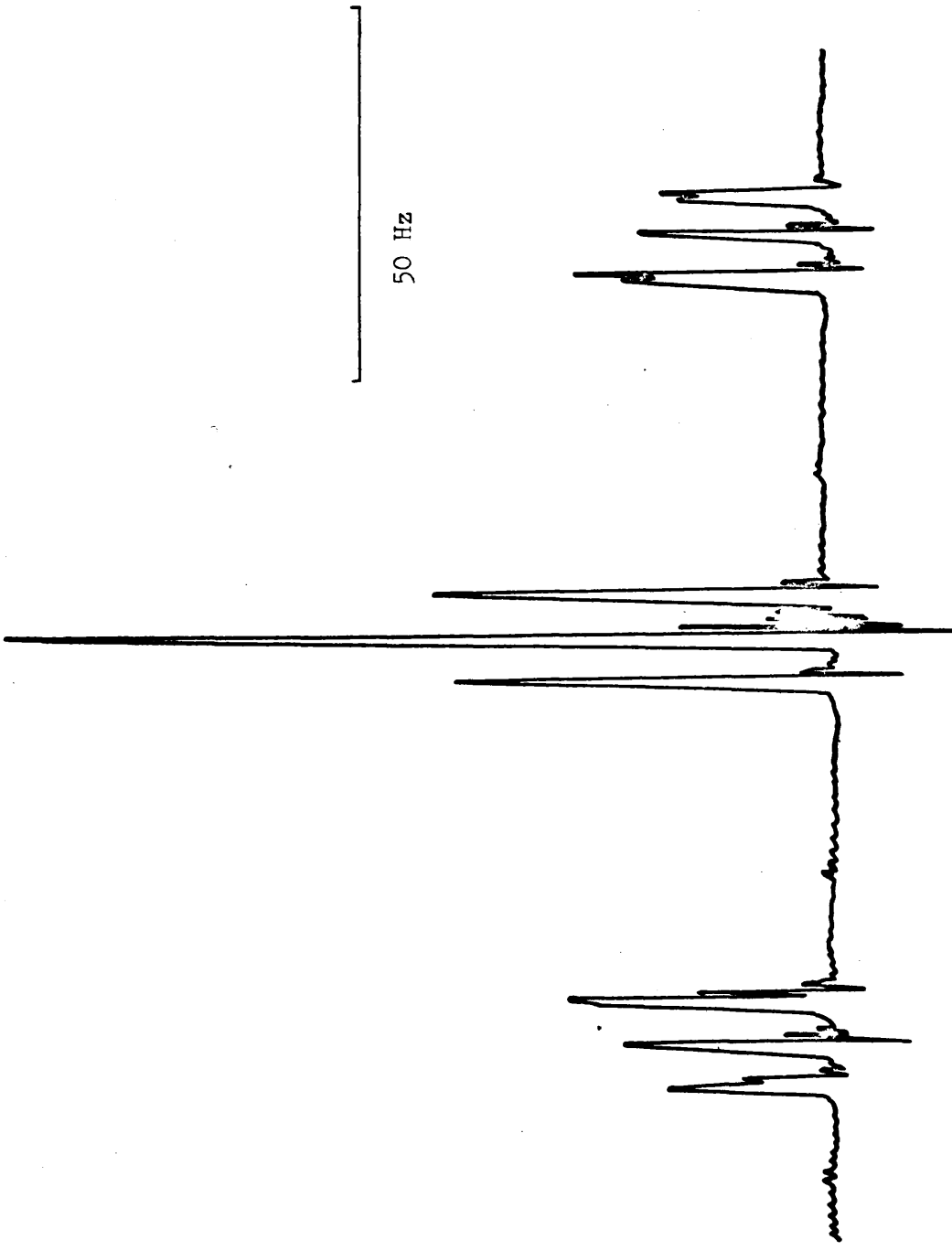


FIGURE 2.6: ^{19}F n.m.r. spectrum of product formulated as CH_2FOCH_2F

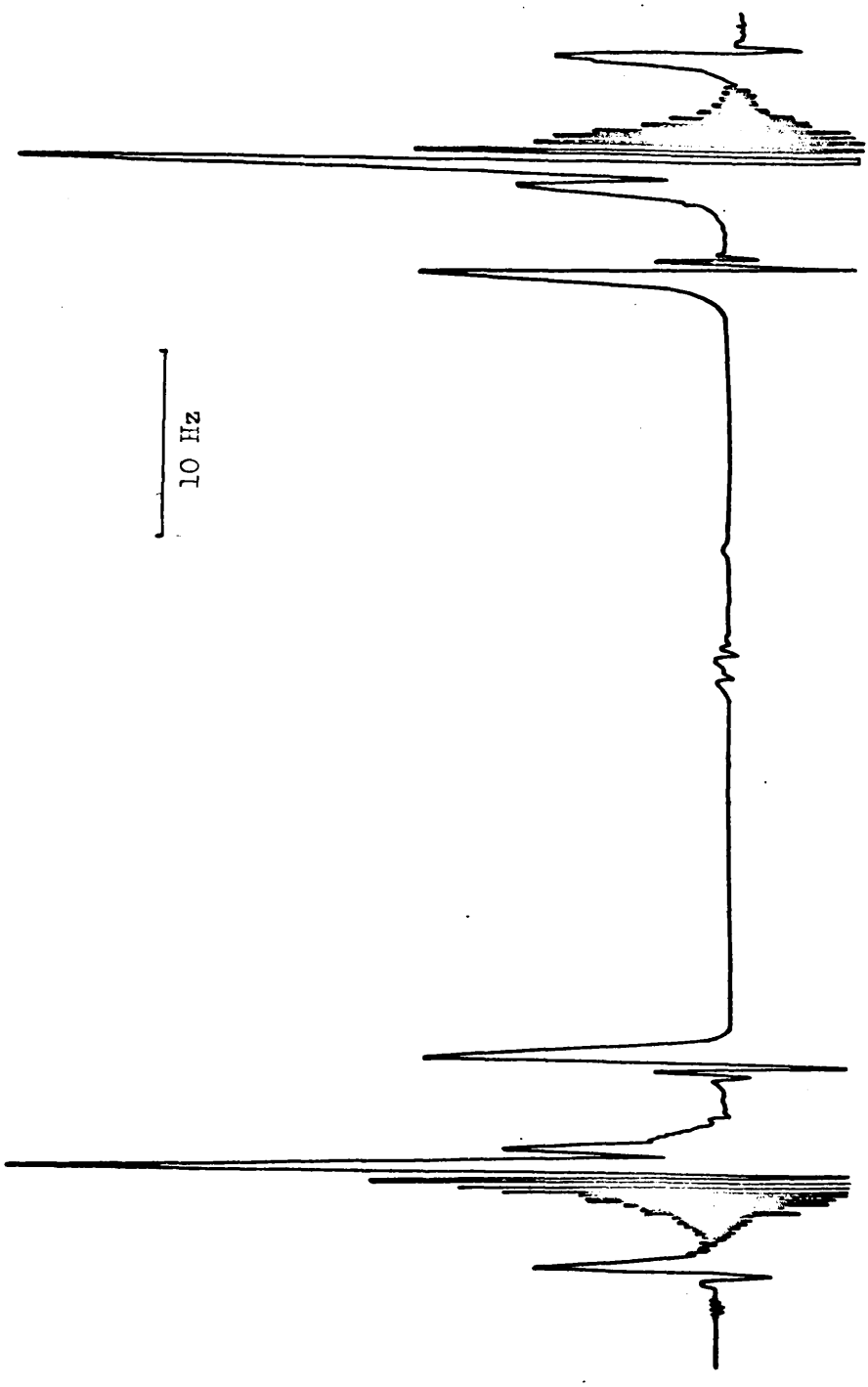


FIGURE 2.7: ^{1}H n.m.r. spectrum of product formulated as CH_2FOCH_2F

TABLE 2.8

R	Ratio [a] $(RO)_2SO:WF_6$	Ratio [a] $ROS(O)F:WF_6$
Me	0.95	- [b]
Me	1.0	1.0
Me	2.4	0.8 [c]
Me	3.3	1.3 [c]
Et	0.8	- [b]
Et	2.3	0.9 [c]
Ph	0.7	0.6 [b]

[a] WF_6 in the ratio is the initial amount used. [b] All the WF_6 did not react. [c] Excess $(RO)_2SO$ observed in the products.

Some typical reactions are described below.

(a) WF_6 (3.4 g, 12 mmoles) dissolved in $(MeO)_2SO$ (1.3 g, 12 mmoles) at -60° giving a pale yellow solution. A smooth reaction occurred at -40° and was complete within 10 minutes giving a white crystalline solid and a colourless supernatant liquid. The latter was removed at -30°, purified by vacuum distillation several times at this temperature, and identified as methyl fluorosulphite, MeOS(O)F (1.1 g, 12 mmoles, yield 100%).

Elemental analysis. Found: C, 12.9; H, 2.8; F, 20.1; S, 32.7%. CH_3FO_2S requires: C, 12.2; H, 3.1; F, 19.4; S, 33.7%.
Molecular weight. Found, 98.5. MeOS(O)F requires, 98.1.
Mass spectrum (source 200°, el. beam 70 eV, relative intensities are in brackets and possible assignments are given in some cases): $^m/_e$, 100(3), $CH_3FO_2{}^{34}S^+$; 99(4), $CH_3FO_2{}^{33}S^+$; 98(37), $CH_3FO_2S^+$; 97(57) $CH_2FO_2S^+$; 81(4); 80(2); 79(75), $CH_3O_2S^+$; 76(4); 70(3); 69(27); 68(70); 67(100) FOS^+; 66(2); 65(4); 64(48), O_2S^+; 51(4); 50(3); 49(7); 48(36), OS^+; 46(2); 45(2). A fragment at $^m/_e$, 110(12) was assigned to $(CH_3O)_2SO$, possibly present as an impurity in this sample. Infrared spectrum (vapour phase, 10 mm, 4000 - 400 cm^{-1}): 3020w, 2960m, 2945w, 1464w, 1266s, 995sh, 986s, 754m, 701s, 590w cm^{-1}.

The ^{19}F n.m.r. spectrum of the neat liquid (CCl_3F ref.) consisted of a quartet (J_{HF} = 1.3 Hz) at -55.6 p.p.m., and the ^1H n.m.r. spectrum consisted of a doublet (J_{HF} = 1.3 Hz) at 6.15τ.

The solid product was purified by vacuum sublimation at 25°, and identified as pentafluoromethoxotungsten(VI), WF_5OMe (3.5 g, 11 mmoles, yield 92%).
Elemental analysis. Found: C, 3.7; H, 1.1; F, 29.3; W, 59.0%. CH_3F_5OW requires: C, 3.9; H, 1.0; F, 30.7; W, 59.3%.
Infrared spectrum (nujol and florube mulls, 4000 - 400 cm^{-1}): 3025w, 2950w, 2825w, 1430m, 1295m, 1110m, 1049m, 1040m, 992s, 680s, 620s, 490s cm^{-1}.

Raman spectra: (solid) 2959w, 2889s, 1441w, 1114sh, 1093s, 708s, 626w, 563m, 363w, 295w cm^{-1}; (in C_6F_6) 2914m, 1165m, 1120w, 724m, 569s, 512w, 485m, 447s, 373s, 302w cm^{-1}. The bands at 373 and 447 cm^{-1} in the latter spectrum may arise from C_6F_6.[176]

WF_5OMe dissolved in C_6F_6 forming a pale yellow solution. N.m.r. spectral data for WF_5OMe in several solvents and in a partially-decomposed melt are summarised in Table 2.9. The ^{19}F n.m.r. spectrum consisted of a doublet and a quintet with relative intensities 4:1, characteristic of an AX_4 spin system. The ^{19}F n.m.r. signals showed further complex splittings ($J \sim 1$ Hz) on an expanded scale. The ^1H n.m.r. spectrum contained a multiplet with a minimum of 5 lines, approximating to a quintet. Reactions occurred when WF_5OMe was dissolved in CH_3CN and C_6F_6 (see below).

/Table 2.9

TABLE 2.9

^{1}H and ^{19}F n.m.r. spectra of WF_5OMe

Solvent	δ_F, p.p.m. (rel.CCl_3F)	J_{FF} Hz	J_{WF} Hz	δ_H τ	J_{HF} Hz	$J_{FF}/\nu_o \delta$
C_6F_6	-118.5 (F_X) - 89.5 (F_A)	66	40 (F_X) 33 (F_A)	4.40	1	0.040
WF_6	-123.5 (F_X) - 86.5 (F_A)	66	41 (F_X)			0.032
CCl_3F	-121.8 (F_X) - [a]	64		4.54	1	
melt[b]	-115.8 (F_X) - 77.6 (F_A)	67	42 (F_X)	4.8	1	0.031

[a] Dilute solution, F_A not observed. [b] Partially decomposed, and ^{19}F n.m.r. spectrum also contained a singlet at -67.2 p.p.m. (J_{WF} = 68 Hz) and a quartet at +270 p.p.m. (J_{HF} = 46 Hz) assigned to WOF_4[35] and MeF[154] respectively.

(b) WF_6 (1.4 g, 4.7 mmoles) and $(MeO)_2SO$ (1.2 g, 11 mmoles) reacted under similar conditions to give MeOS(O)F (0.4 g, 4.5 mmoles), unreacted $(MeO)_2SO$ (0.2 g, 1.5 mmoles) and methyl fluoride (trace, identified by i.r.[105]). The involatile residue was a pale orange liquid, which did not contain WF_5OMe. Elemental analysis gave: C, 7.26; H, 1.00; S, 2.66; F, 28.1; W, 58.3% (ratio, F:W = 4.7:1). (A sample of the same product from another reaction, using similar quantities of reactants, gave: C, 6.65; H, 1.78; S, 0.24; F, 20.9%) The ^{19}F n.m.r. spectrum of the neat liquid (CCl_3F ref.) consisted of a major signal at -60.8 p.p.m. (doublet, J_{FF} = 59 Hz, J_{WF} = 50 Hz) and signals of less intensity at +145.6 p.p.m. (multiplet, minimum of 7 lines, J_{FF} = 59 Hz, J_{WF} = 50 Hz) and -65.2 p.p.m. (singlet, broadened). The doublet and multiplet had relative intensities ca. 8:1. The ^1H n.m.r. spectrum consisted of a major singlet at 5.65τ and minor singlets at 4.60τ, 4.77τ and 5.71τ.

(3) Tungsten hexafluoride and diethyl sulphite

(a) A vigorous reaction occurred between WF_6 (3.6 g, 12 mmoles) and diethyl sulphite (1.4 g, 10 mmoles) at -40°. After 30 minutes the temperature was raised to 20° to ensure complete reaction. The products were a pale yellow solid and a colourless liquid.

The small quantity of material volatile at -60° was identified by i.r. as a mixture of WF_6,[101] EtF[177] and SO_2.[102] The fraction volatile at 25° was a colourless liquid identified as ethyl

fluorosulphite, EtOS(O)F (1.0 g, 9.1 mmoles, yield 91%).

Molecular weight. Found, 111.8. EtOS(O)F requires, 112.1.

Mass spectrum (source 200°, el. beam 70 eV, prominent peaks only, with relative intensities in brackets): $^{m}/e$ 115(1), impurity?; 113(0.5); $C_2H_4FO_2{}^{34}S^+$; 112(0.5), $C_2H_4FO_2{}^{33}S^+$ and $C_2H_5FO_2{}^{32}S^+$; 111(9), $C_2H_4FO_2{}^{32}S$; 110(1); 99(5); 98(2); 97(11); $CH_2FO_2S^+$; 93(3); 92(4); 85(11); 83(5), FO_2S^+; 82(8); 80(1); 78(6); 76(7); 74(3); 71(2); 69(5); 68(11); 67(17), FOS^+; 66(9); 65(8); 64(19), O_2S^+; 59(6); 51(5); 50(6); 49(7); 48(100), OS^+; 47(5); 46(4); 45(17); 43(9); 42(7); 41(2); 40(4). Some of the assignments were confirmed by mass measurements (Table 2.10).

TABLE 2.10

$^{m}/e$	Ion	Mass	Theory
113	$C_2H_4FO_2{}^{34}S^+$	112.98788	112.98739
112	$C_2H_4FO_2{}^{33}S^+$	111.99144	111.99099
	$C_2H_5FO_2{}^{32}S^+$	111.99904	111.99942
111	$C_2H_4FO_2{}^{32}S^+$	110.99161	110.99160

Infrared spectrum (vapour phase, 5 mm, 4000 - 400 cm^{-1}): 2992m, 2970sh, 2958sh, 2910sh, 1442w, 1400w, 1390w, 1372w, 1260s, 1110w, 1062sh, 1055m, 1044m, 1000sh, 994s, 910s, 875w, 860w, 735sh, 696s, 590w cm^{-1}.

The ^{19}F n.m.r. spectrum of the neat liquid (CCl_3F ref.) consisted of a multiplet with a minimum of 3 lines ($J \sim 1.3$ Hz) at -59.8 p.p.m., and the ^{1}H n.m.r. spectrum consisted of two multiplets at 5.65 τ and 8.65τ ($J_1 = 7$ Hz, $J_2 \sim 1.3$ Hz) with relative intensities 2:3.

The solid product decomposed at 20°, with the evolution of EtF (identified by i.r.[177]).

Elemental analysis. Found W, 62.4%. WF_5OEt requires W, 56.8; WOF_4 requires W, 66.6%.

(b) WF_6 (4.6 g, 15 mmoles) and $(EtO)_2SO$ (4.8 g, 34 mmoles) reacted under similar conditions to give EtOS(O)F (1.5 g, 13 mmoles), EtF (trace), unreacted $(EtO)_2SO$ (0.4 g, 3.2 mmoles) and a viscous orange liquid. The ^{19}F n.m.r. spectrum of a neat sample of the latter (CCl_3F ref.) consisted of a major signal at -61.2 p.p.m. (doublet, $J_{FF} = 58$ Hz, $J_{WF} = 72$ Hz) and signals of less intensity at -66.1 p.p.m. (broadened singlet, $\frac{1}{2}$ height width = 19 Hz, $J_{WF} = 69$ Hz), +144.9 p.p.m. (multiplet, minimum of 7 lines, $J_{FF} = 58$ Hz, $J_{WF} = 50$ Hz) and +210 p.p.m. (multiplet, minimum of 8 lines, $J \sim 25$ Hz). The doublet and multiplet at +144.9 p.p.m. had relative intensities ca. 8:1. The ^{1}H n.m.r. spectrum consisted of signals at 4.70τ (broadened multiplet, minimum of 5 lines, $J = 7$ Hz), 5.60τ (multiplet, minimum of 8 lines, $J = 7$ Hz), and 8.76 τ (multiplet, minimum of 8 lines). Elemental analysis gave: C, 9.76; H, 1.94: F, 17.7; S, 12.5; W, 51.9% (ratio F:W = 3.3:1).

(4) Tungsten hexafluoride and diphenyl sulphite

A dry reaction flask was charged with $(PhO)_2SO$ (2.7 g, 11.5 mmoles) in a dry-box, evacuated, and WF_6 (4.8 g, 16 mmoles) was added. A smooth reaction occurred at 20° and appeared to be complete after 15 minutes, yielding a dark red solution from which a dark red solid separated.

The fraction volatile at -80° was identified from its infrared spectrum as a mixture of SiF_4 [103] (trace) and WF_6. [101] Unreacted WF_6 (1.4 g, 4.5 mmoles) was completely removed at -25°, and after removal of the material volatile at 20°, a dark red solid remained. This was purified by vacuum sublimation at 60° (10^{-4} mm), and identified as pentafluorophenoxotungsten(VI), WF_5OPh (4.1 g, 11.0 mmoles, yield 96%).

Elemental analysis. Found: C, 21.1; H, 1.68; F, 24.9; W, 48.5%. $C_6H_5F_5OW$ requires: C, 19.4, H, 1.35; F, 25.5; W, 49.4%.

Infrared spectrum (florube and nujol mulls, 4000 - 400 cm^{-1}): 3102w, 3070w, 1875w, 1590w, 1481m, 1462w, 1290w, 1205m, 1155w, 1090w, 1065w, 1018w, 940m, 915w, 751s, 712s, 665s, 640s, 512w, 489m cm^{-1}.

The ^{19}F n.m.r. spectrum (Fig. 2.2) was characteristic of an AB_4 system [141] which approximated to AX_4 (the signals from F_{eq} and F_{ax} had, however, relative intensities ca. 5:1), and a first-order analysis gave the following parameters (C_6F_6 solution, CCl_3F ref.):

δF_X = -131.9 p.p.m., J_{FF} = 64 Hz, J_{WF} = 39 Hz; δF_A = -118.6 p.p.m.; $J/\nu_o \delta$ = 0.088. All the signals showed further complex splittings (J~1 Hz) on an expanded scale. The ^1H n.m.r. spectrum consisted of a complex pattern of 6 lines, 2.15-2.85τ, each of which showed further splittings on an expanded scale.

The product volatile at 20° contained a small amount of WF_5OPh. The addition of a small quantity of trimethylamine yielded an involatile red solid (probably a WF_5OPh-Me_3N adduct) and a colourless liquid. The latter was identified as phenyl fluorosulphite, PhOS(O)F (1.6 g, 10 mmoles, yield 88%).

Elemental analysis. Found, C, 40.7; H, 4.92; F, 11.3; S, 21.0%. $C_6H_5FO_2S$ requires, C, 45.0; H, 3.15; F, 11.9; S, 20.0%.

Infrared spectrum (liquid film, 4000 - 400 cm^{-1}): 3065w, 3045sh, 1945w, 1872w, 1785w, 1730w, 1597sh, 1589m, 1489s, 1456m, 1308w, 1276sh, 1265s, 1180s, 1144s, 1072m, 1025m, 912m, 855s, 825sh, 786s, 721s, 744m, 717s, 687s, 622m, 599w, 510m, 487w, 455m, 405m cm^{-1}.

The ^{19}F n.m.r. spectrum of the neat liquid (CCl_3F ref.) consisted of a single resonance at -64.5 p.p.m. which showed complex splittings on an expanded scale. The ^1H n.m.r. spectrum consisted of a multiplet at 2.87τ. The n.m.r. and i.r. spectra of this product are in good agreement with previously reported values for PhOS(O)F.[147] Its slow decomposition at 20° may account for the discrepancies in the analytical data.

(5) Tungsten hexafluoride and sulphur trioxide

(a) WF_6 (2.7 g, 9.2 mmoles) and SO_3 (0.52 g, 6.5 mmoles) reacted moderately at 20° to give a pale yellow viscous liquid. The ^{19}F n.m.r. spectrum (CCl_3F ref.) of a sample of the reaction mixture after 2 hours consisted of a major signal characteristic of WF_6 (J_{WF} = 44 Hz, cf. Table 1.5) and signals of much less intensity at -181 p.p.m. (broad, unresolved, $\frac{1}{2}$ height width approx. 100 Hz), -50.9, -50.4, -49, -45.4, -44.3 and -24.5 p.p.m. (all singlets). From the remainder of the reaction mixture the fraction volatile at 25° (mainly WF_6, identified by i.r.[101]) was removed, yielding a pale yellow viscous liquid. Partial elemental analysis gave: F, 21.1, S, 11.4%. This product hydrolysed readily, yielding WO_3, but tungsten analyses were not performed.

WF_5SO_3F requires, F, 30.2; S, 8.49; W, 48.7%.

$WF_4(SO_3F)_2$ requires, F, 24.9; S, 14.0; W, 40.2%.

$WF_3(SO_3F)_3$ requires, F, 21.2; S, 17.9; W, 34.2%.

$WF_2(SO_3F)_4$ requires, F, 18.4; S, 20.8; W, 29.8%.

(b) WF_6 (7.4 g, 25 mmoles) and sulphur trioxide (4.9 g, 61 mmoles) reacted vigorously at 20° to give a pale yellow viscous liquid. The ^{19}F n.m.r. spectrum (CCl_3F ref.) of a sample of the reaction mixture after 2 hours consisted of a major signal characteristic of WF_6 (Table 1.5), and less intense signals at -180.2 p.p.m. (broad, unresolved), -122.7 p.p.m. (broad, unresolved, $\frac{1}{2}$ height width approx.

100 Hz), -50.4 p.p.m. (multiplet minimum of 3 lines), -50 p.p.m. (singlet), -48.6 p.p.m. (singlet), and -42.5 p.p.m. (multiplet with minimum of 8 lines, and structure similar to the calculated second order AB_4 spectrum with $J/\nu_o \delta$ in the range 1.00-5.00, see figure 2.3).

The fraction volatile at 25° (2 g) was a colourless liquid, and was identified from its infrared spectrum as a mixture of WF_6[101] and pyrosulphuryl fluoride, $S_2O_5F_2$.[114] The ^{19}F n.m.r. spectrum (CCl_3F ref.) contained a major signal characteristic of WF_6 (Table 1.5) and signals of less intensity at -49.6, -48.2 and 23.5 p.p.m. (all singlets). The identification of pyrosulphuryl fluoride is summarised in Table 2.11.

The involatile product was a pale yellow viscous liquid. Elemental analysis gave: F, 19.7; S, 8.88; W, 45.0%.

TABLE 2.11

	δF p.p.m. (rel. CCl_3F)	ν(S=O)	ν(S-F)	Ref.
$S_2O_5F_2$	-48.8	1513	872	114
		1248	824	
product	-48.2	1515	875	
		1248	830	

(6) Tungsten hexafluoride and dimethyl sulphone

Dimethyl sulphone did not dissolve in WF_6, and no reaction was observed at 75° (60 hours).

(7) Tungsten hexafluoride and trimethyl phosphite

These reactions were extremely vigorous, and careful temperature control was necessary. Explosions occurred in some reactions where equimolar quantities of reactants were used.

(a) WF_6 (1.3 g, 4.5 mmoles) and $P(OMe)_3$ (1.8 g, 15 mmoles) formed a bright yellow solution at -80°. The reaction mixture was allowed to warm from -80° to 0° over 12 hours, and the yellow colour was discharged, yielding a colourless liquid. The identification of the products is summarised in Table 2.12.

Fraction (i), volatile at -25°, was a mixture of dimethyl fluorophosphite, $PF(OMe)_2$ (4.5 mmoles) and unreacted $P(OMe)_3$ (2.4 mmoles). These were not separated, and the composition of the mixture was estimated from the intensities of the ^1H n.m.r. signals.

Fraction (ii), volatile at 25°, was identified as dimethyl methylphosphonate, $(MeO)_2P(O)Me$, with small amounts of oxotetrafluoro(dimethyl methylphosphonate)tungsten(VI), $WOF_4.OP(OMe)_2Me$, and methyl methylphosphonofluoridate, $MeP(O)(F)OMe$. The ^1H n.m.r. signals of the latter product were not resolved.

Fraction (iii), an involatile liquid, contained $(MeO)_2P(O)Me$ (55%), $WOF_4.OP(OMe)_2Me$ (25%), and trimethoxymethyl-/phosphonium oxopentafluoro-

TABLE 2.12

(Literature values are in Table 2.5)

Fraction	Product	δ_H (OMe) τ	δ_H (Me) τ	δ_F p.p.m. (rel. CCl_3F)	J_{PH} (OMe) Hz	J_{PH} (Me) Hz	J_{PF} Hz	J_{WF} Hz	J_{FF} Hz	J_{HF} Hz
(i)	$P(OMe)_3$ (unreacted)	6.53			10.6					
(neat)	$PF(OMe)_2$	6.43		+61.6	10.4		1209			0.6
(ii)	$(MeO)_2P(O)Me$	6.36	8.60		10.8	17.0				
(neat)	$MeP(O)(F)OMe$			+63.1			1032			
	$WOF_4.OP(OMe)_2Me$	6.10	8.19	-61.5	12.0	18.3	1.7	73		
(iii)	$(MeO)_2P(O)Me$	6.38	8.61		11.3	17.6				
(neat)	$WOF_4.OP(OMe)_2Me$	6.15	8.27	-60.7	12.0	18.4		69		
	$(MeO)_3PMe^+WOF_5^-$	5.85	7.72	-48.6(F_X)	11.7	18.4		71(F_X)	52	

tungstate(VI), $(MeO)_3PMe^+$ WOF_5^- (20%) (the quintet of the AX_4 ^{19}F n.m.r. spectrum was too weak to be detected). Dimethyl methylphosphonate could not be completely removed from the products by vacuum distillation. On heating this fraction to 160° (12 hours) methyl fluoride was evolved (identified by i.r.[105]).

(b) A large reaction vessel (200 ml) was used to avoid explosion. A mixture of WF_6 (0.72 g, 2.4 mmoles) and $P(OMe)_3$ (0.26 g, 2.1 mmoles) was bright yellow at -80°. At 0° an orange oil was formed, and this decomposed rapidly yielding a colourless liquid and a white solid. The reaction was complete in 15 minutes. The identification of the products is summarised in Table 2.13.

The fraction volatile at 25° (0.12 g) contained MeF, WF_5OMe (only the doublet of the AX_4 ^{19}F n.m.r. spectrum was observed, the quintet being too weak for detection), and unreacted WF_6 (trace). The ^{19}F n.m.r. spectrum also contained a signal in the region characteristic of WOF_4 and its complexes (cf. Table 1.3). The ^1H n.m.r. spectrum contained signals whose splittings and intensity ratios were consistent with MeP(O)(F)OMe, but the chemical shift of the ^{19}F n.m.r. signals in the P-F region (doublet, J = 965 Hz, each peak showing further, unresolved splittings) was 16.2 p.p.m. downfield from the literature value for MeP(O)(F)OMe, and J_{PF} was 74 Hz less than that of MeP(O)(F)OMe.[137] These discrepancies might be accounted for by the presence of the complex oxotetrafluoro(methyl methylphosphono-

TABLE 2.13

(Literature values are in Table 2.5)

Product (CCl_3F soln.)	δ_H (OMe) τ	δ_H (Me) τ	δ_F p.p.m. (rel. CCl_3F)	J_{PH} (OMe) Hz	J_{PH} (Me) Hz	J_{PF} Hz	J_{WF} Hz	J_{FF} Hz	J_{HF} Hz
WF_6 (unreacted)			-161.6						
WF_5OMe	4.48		-120.4(F_X)					62	
$WOF_4.OP(F)(OMe)Me$ (?)	6.02	8.22	-61.9(WF) +45.8(PF)	12	19.5	965(P-F)	70		6.6(FPCH) 0.9(FPOCH)
MeF		5.85	+273.2						47

TABLE 2.14

(Literature values are in Table 2.5)

Product (CCl_3F soln.)	δ_H (OMe) τ	δ_H (Me) τ	δ_F p.p.m. (rel. CCl_3F)	J_{PH} (OMe) Hz	J_{PH} (Me) Hz	J_{PF} Hz	J_{HF} (OMe) Hz	J_{HF} (Me) Hz	J_{WF} Hz
$MeP(O)(F)OMe$	6.21	8.47	+62.0	11.6	18.9	1038	0.8	5.8	
$(MeO)_2P(O)Me$ (unreacted)	6.31	8.61		11.3	18.4				
$WOF_4.OP(OMe)_2Me$			-61.2			2			72
WF_5OMe	4.49						1		
MeF		5.86						47	

fluoridate)tungsten(VI), $WOF_4.OP(F)(OMe)Me$, but the evidence for this is not conclusive.

Other volatile products giving rise to weak ^1H n.m.r. signals at 2.74τ , 2.90τ , 7.72τ , 8.56τ (all single lines), 8.73τ (multiplet) and 9.09τ (multiplet) were not identified.

The involatile solid-liquid product was not investigated, but was similar in appearance to that obtained in (a).

(8) Tungsten hexafluoride and dimethyl methylphosphonate

WF_6 (1.1 g, 3.7 mmoles) and $(MeO)_2P(O)Me$ (0.81 g, 6.5 mmoles) reacted vigorously at 25°, yielding a white solid and a colourless viscous liquid. The identification of the products is summarised in Table 2.14.

The fraction volatile at 20° (0.05 g) contained $MeP(O)(F)OMe$ and unreacted $(MeO)_2P(O)Me$. Other products giving rise to ^1H n.m.r. signals at 9.03τ (singlet) and 9.26τ (multiplet) were not identified.

The involatile solid-liquid residue was sparingly soluble in C_6F_6. The ^1H n.m.r. spectrum contained signals characteristic of free and coordinated $(MeO)_2P(O)Me$, and the ^{19}F n.m.r. spectrum contained a major signal assigned to $WOF_4.OP(OMe)_2Me$, and weaker unassigned singlets at -63.2 and -50.2 p.p.m. (CCl_3F ref.).

In a separate experiment with similar quantities of reactants the ^1H n.m.r. spectrum of the volatile fraction contained signals characteristic of WF_5OMe and MeF in addition to those described above,

but the solution was too dilute for satisfactory resolution of the ^{19}F n.m.r. signals.

(9) Tungsten hexafluoride and dimethyl phosphite

WF_6 (2.3 g, 7.8 mmoles) and dimethyl phosphite (0.93 g, 8.5 mmoles) formed a yellow solution at -80°, and after several minutes a vigorous reaction occurred. On warming to 20° two colourless immiscible liquids were obtained. The infrared spectrum of the fraction volatile at -120° (0.5 g) consisted of absorptions characteristic of phosphorus trifluoride[178] and SiF_4[103] (trace). Molecular weight: found, 91.8. PF_3 requires, 88.0; SiF_4 requires 104.1.

The less volatile fractions rapidly turned blue, and were not examined. Some etching of the glassware was observed.

Thermal decomposition of Pentafluoromethoxotungsten(VI)

(a) Methyl fluoride (identified by i.r.[105]) was evolved from WF_5OMe at 20° (7 days).

(b) WF_5OMe (2.3 g, 7.6 mmoles) melted at 85°, and began to decompose at 120°, turning pale yellow. The temperature was allowed to rise to 150° (2 hours). The volatile material (methyl fluoride, identified by i.r.[105]) was removed from time to time to avoid excessive pressure in the reaction vessel, and some WF_5OMe was lost by sublimation. On cooling the contents of the reaction vessel to 20° a white solid was obtained. This was identified as predominantly tungsten oxotetra-

fluoride, WOF_4 (1.6 g, 5.8 mmoles, yield 76%). No attempt was made to purify the product by sublimation.

Elemental Analysis. Found: C, 0.2; H, 0.2; F, 26.6; W, 65.8%. WOF_4 requires, F, 27.5; W, 66.6%.

The infrared spectrum (nujol mull, 4000-400 cm^{-1}) contained absorptions at 1045s, 1028sh, 715s, 660s, 628s, 550s, 462s and 398w cm^{-1} characteristic of WOF_4.[50] The following absorptions were attributed to impurities: 2096m, 1538w, 1253w, 1165w, 997sh (WF_5OMe?), 988m (WF_5OMe?), 919m, 900sh, 833wbr, 798w cm^{-1}.

Thermal decomposition of pentafluorophenoxotungsten(VI)

WF_5OPh melted at 80°, and after 30 hours at 180° a brown solid was obtained. There was considerable etching of the glass vessel. The infrared spectrum of the volatile material consisted of absorptions characteristic of SiF_4,[103] and weak unassigned absorptions at 1515m, 1470sh, 1455s, 1385w and 1365w cm^{-1}.

Molecular weight: found, 103.6. SiF_4 requires, 104.1.

Reactions of Pentafluoromethoxotungsten(VI)

(1) With dimethyl sulphite.

WF_5OMe (1.0 g, 3.1 mmoles) dissolved slowly in $(MeO)_2SO$ (0.5 g, 4.5 mmoles) yielding a colourless liquid whose ^{19}F n.m.r. spectrum after 30 minutes (CCl_3F ref., lettering as in figure 2.4) consisted of signals at -115.8 p.p.m. (A, doublet, J_{FF} = 67 Hz), -65.8 p.p.m. (B, single line, J_{WF} = 68 Hz), -63.2 p.p.m. (C, triplet, J_{FF} = 66 Hz),

-61.5 p.p.m. (D, doublet, J_{FF} = 59 Hz, J_{WF} = 71 Hz), -55.6 p.p.m. (E, quartet, J = 1 Hz), -43.0 p.p.m. (F, triplet, J_{FF} = 66 Hz), + 145.8 p.p.m. (G, multiplet, minimum of 5 lines, J_{FF} = 59 Hz) and + 271.3 p.p.m. (H, quartet, J = 45 Hz). Signals C and F were of equal intensity, and D and G had relative intensities ca. 8.5:1. The ^{1}H n.m.r. spectrum (figure 2.5) contained signals at 4.19 τ (J, multiplet, minimum of 5 lines, J = 1 Hz), 4.63 τ (K, multiplet, minimum of 5 lines, J = 1.2 Hz), 5.39 τ (L, single line), 5.57 τ (M, single line), 5.69 τ (N, single line), 6.14 τ (multiplet, which, on an expanded scale, showed a doublet, O, J = 1.5 Hz, superimposed on a single line of less intensity) and 6.41 τ (P, singlet). The ^{19}F n.m.r. spectrum after 1 hour showed a significant decrease in intensity of signal A, and after 12 days signals A, C and F were absent, while D and G had increased in intensity. The ^{1}H n.m.r. spectrum after 12 days also showed minor changes. Signal J was absent, K showed a significant reduction in intensity, a new signal had appeared at 5.03 τ (Q, broadened multiplet), and M and N were replaced by a major signal at 5.62 τ (single line).

It is possible that some of the increase in intensity of the signals characteristic of $W_2O_2F_9^-$ (i.e. D and G) was due to hydrolysis, though there was no evidence of this.

(2) With trimethyl phosphite

WF_5OMe (0.34 g, 1.1 mmoles) and $P(OMe)_3$ (0.19 g, 1.5 mmoles)

initially formed a pale yellow solution. Reaction was rapid at 20° yielding a white solid and a colourless liquid. The identification of the products is summarised in Table 2.15.

The fraction volatile at 25° (0.28 g) contained dimethyl methylphosphonate. A major volatile product, giving a singlet in the ^{1}H n.m.r. spectrum at 6.82 τ, may have been dimethyl ether (Me_2O, 6.76 τ [155]). This fraction did not show any ^{19}F n.m.r. signals.

The involatile oily solid dissolved readily in CD_3CN and was a mixture of trimethoxymethylphosphonium oxopentafluorotungstate(VI), $(MeO)_3PMe^+ WOF_5^-$, (95%), and oxotetrafluoro(dimethyl methylphosphonate)-tungsten(VI), $WOF_4.OP(OMe)_2Me$, (5%).

Elemental analysis. Found: C, 10.9; H, 2.95; F, 19.5; P, 7.93; W, 37.3%. $(MeO)_3PMe^+ WOF_5^-$ ($C_4H_{12}O_4F_5PW$) requires: C, 11.1; H, 2.79; F, 21.9; P, 7.14: W, 42.4%.

The ^{19}F n.m.r. spectrum of $(MeO)_3PMe^+ WOF_5^-$ consisted of a doublet and a quintet with relative intensities 4:1, characteristic of an AX_4 system, and the parameters were very similar to those reported for the WOF_5^- anion in $Pr_4N^+ WOF_5^-$.[35] The ^{1}H n.m.r. spectrum consisted of two doublets (relative intensities 3:1), whose chemical shifts were characteristic of MeO and Me groups respectively, the spectral parameters being very similar to those reported for the $(MeO)_3PMe^+$ cation in $(MeO)_3PMe^+ PF_6^-$.[137]

The ^{19}F n.m.r. spectrum of the involatile product in CD_3CN was

TABLE 2.15

(Literature values are in Table 2.5)

Product	Solvent	δ_H (OMe) τ	δ_H (Me) τ	δ_F p.p.m. (rel. CCl_3F)	J_{PH} (OMe) Hz	J_{PH} (Me) Hz	J_{WF} Hz	J_{FF} Hz	J_{PF} Hz
$(MeO)_2P(O)Me$	CCl_3F	6.39	8.71		11.2	17.9			
$WOF_4 \cdot OP(OMe)_2Me$ (5%)	CD_3CN			-61.7					1.7
$(MeO)_3PMe^+WOF_5^-$ (95%)		5.92	7.89	-49.8(F_X) +84.2(F_A)	11.4	17.4	72(F_X)	53	
$(MeO)_3PMe^+WOF_5^-$ (20%)	CD_3CN			-48.4(F_X)			72(F_X)	53	
$WOF_4 \cdot OP(OMe)_2Me$ (80%)				-60.6			71		1.7

re-run after 2 months at 20°. The same signals were observed, but the composition of the mixture was, $(MeO)_3PMe^+$ WOF_5^- (20%), $WOF_4.OP(OMe)_2Me$ (80%).

In a separate experiment in which the temperature of the reaction was not carefully controlled, WF_5OMe (2.3 g, 7.6 mmoles) and $P(OMe)_3$ (1.4 g, 11.5 mmoles) gave a mixture of $(MeO)_3PMe^+$ WOF_5^- (35%) and $WOF_4.OP(OMe)_2Me$ (65%) as the involatile products.

(3) With pyridine

Reaction of WF_5OMe (6 g, 19 mmoles) and pyridine (5 ml) in C_6F_6 (10 ml) at 20° yielded, after removal of the unreacted pyridine and C_6F_6, a dark brown solid (8.2 g) which analysed as WF_5OMe,1.3py. Elemental analysis. Found: C, 21.2; H, 2.22; F, 21.9; N, 4.29; W, 44.6%. WF_5OMe,1.3py requires: C, 21.8; H, 2.32; F, 23.0; N, 4.40; W, 44.5%. I.r.spec. (nujol and florube mulls, 4000-400 cm^{-1}): 3240w, 3170sh, 3140m, 3080s, 2980w, 2860w, 1945w, 1855w, 1638s, 1612m, 1589w, 1488s, 1462sh, 1453s, 1245w, 1214m, 1195s, 1168m, 1138w, 1070m, 1060sh, 1050m, 1030w, 1020m, 975s, 925m, 800w, 765s, 678s, 585s cm^{-1}.

(4) With benzene

WF_5OMe was soluble in C_6H_6 to yield a pale yellow solution which darkened after 30 minutes, forming eventually a green oil and a blue solid. Considerable etching of the glass vessel was observed, and the infrared spectrum of the volatile materials consisted of absorptions characteristic of SiF_4,[103] benzene[102] and toluene (?).[102a] A signal

at 7.83τ in the ^{1}H n.m.r. spectrum of the volatile materials suggested the presence of toluene (reported at 7.67τ [155]).

The ^{19}F n.m.r. spectrum of the green oil consisted of a single broad resonance at -68 p.p.m. (CCl_3F ref.) with satellite peaks from $^{19}F - ^{183}W$ coupling of 70 Hz.

(5) With dimethyl ether

WF_5OMe and Me_2O did not react at 25°.

WF_5OMe (7.4 g, 24 mmoles) and Me_2O (1.4 g, 30 mmoles) were allowed to react at 135° for 12 hours in a stainless-steel bomb. The fraction volatile at -80° was identified by its infrared spectrum as methyl fluoride.[105] The fraction volatile at 20° was a small quantity of colourless liquid which hydrolysed rapidly in H_2O to give WO_3. A brown oil remained in the bomb.

(6) With diethyl ether

WF_5OMe (3.8 g, 12 mmoles) and Et_2O (0.9 g, 12 mmoles) reacted at 25°, slowly at first, and then vigorously, yielding two immiscible, colourless liquids. The reaction was complete after 1 hour.

The fractions volatile at -100° and 0° were identified by their infrared spectra as methyl fluoride[105] (4 mmoles) and Et_2O[102] (7.2 mmoles) respectively.

The involatile product was a colourless liquid which solidified after several hours at 25°. Elemental analysis gave (two samples, from separate reactions): C, 9.85, 9.28; H, 2.37, 2.21; F, 21.6, 21.7;

W, 54.3, 54.3% (ratio C:H:F:W = 5:15:8:2). Infrared spectrum (nujol and florube mulls, 4000-400 cm^{-1}): 3078w, 3000s, 2300w, 2045m, 1462sh, 1450s, 1392s, 1308m, 1242w, 1210w, 1187m, 1168m, 1150w, 1130w, 1090m, 1029sh, 1018s, 969s, 938m, 925m, 860m, 830m, 796m, 716s, 650m, 630m, 460s, 435s cm^{-1}.

The ^{19}F n.m.r. spectrum of this product (neat liquid, spectrum obtained before sample had solidified, CCl_3F ref.) consisted of a minor signal at -65.5 p.p.m. (single line) and major signals at -62.5 p.p.m. (doublet, J_{FF} = 59 Hz, J_{WF} = 72 Hz) and +147.6 p.p.m. (multiplet, minimum of 7 lines, J_{FF} = 59 Hz J_{WF} = 50 Hz) with relative intensities ca. 8:1. The ^{1}H n.m.r. spectrum consisted of major signals at 5.38τ (multiplet, minimum of 8 lines, approximating to a quartet of doublets, J = 7.4 and 2.6 Hz) and 8.46τ (multiplet, minimum of 6 lines, approximating to a triplet of doublets, J = 7.4 and 1.2 Hz), with relative intensities 2:3, and other signals at 5.75 τ 5.84 τ , 6.75τ (all single lines), and 8.87τ (multiplet, minimum of 6 lines approximating to a triplet of doublets, J = 7.1 and 1.8 Hz).

(7) With acetonitrile

WF_5OMe dissolved readily in deuteroacetonitrile with evolution of heat yielding a bright yellow solution whose ^{19}F n.m.r. spectrum (CCl_3F ref.) consisted of signals at -62.5 p.p.m. (doublet, J_{FF} = 60 Hz, J_{WF} = 68 Hz) and -47.3 p.p.m. (doublet, J_{FF} = 53 Hz, J_{WF} = 73 Hz) characteristic of WOF_5^- and $W_2O_2F_9^-$ (Table 1.3) the quintet of WOF_5^-

and the nonet of $W_2O_2F_9^-$ being too weak to be detected.

CHAPTER THREE

THE FLUORINATION OF SOME ORGANOSILICON COMPOUNDS WITH TUNGSTEN HEXAFLUORIDE

THE PREPARATION AND PROPERTIES OF ALKOXY AND PHENOXY TUNGSTEN(VI) FLUORIDES

Introduction

The reactions of alkoxysilanes and siloxanes with Lewis acids are very different from their reactions with Lewis bases.[179] With typical Lewis acids, such as boron, aluminium and phosphorus trihalides, cleavage of the silicon oxygen-bond occurs:

$$\text{e.g.} \quad H_3SiOMe + BF_3 \longrightarrow H_3SiF + MeOBF_2$$

Disiloxane reacts in a similar manner:

$$(SiH_3)_2O + BF_3 \longrightarrow H_3SiF + H_3SiOBF_2$$

In this case[180] H_3SiOBF_2 decomposes appreciably:

$$3H_3SiOBF_2 \longrightarrow 3H_3SiF + BF_3 + B_2O_3$$

In the presence of typical Lewis bases, such as ammonia and trimethylamine, both $(SiH_3)_2O$ and H_3SiOMe undergo condensation and redistribution reactions respectively in the liquid phase:

$$2(SiH_3)_2O \longrightarrow (SiH_3O)_2SiH_2 + SiH_4$$

$$2H_3SiOMe \longrightarrow (MeO)_2SiH_2 + SiH_4 \quad .$$

The fluorination of organosilicon compounds with sulphur tetrafluoride has received some attention. The Si-O-Si bridges in siloxanes are cleaved with the formation of Si-F bonds, and from silanols and silanediols, fluorosilanes and difluorosilanes respectively are obtained. Alkoxysilanes yield the corresponding fluorosilane, alkyl fluoride and dialkyl sulphite:[181]

$$\text{e.g.} \quad Me_2Si(OEt)_2 + 2SF_4 \xrightarrow{20^\circ} Me_2SiF_2 + 2SOF_2 + 2EtF$$

$$Me_2Si(OEt)_2 + SOF_2 \longrightarrow Me_2SiF_2 + (EtO)_2SO \quad .$$

Confirmation of the latter reaction comes from a separate study of the reactions of thionyl fluoride with alkoxysilanes.[182] The Si-OH groups of silanols and silandiols react readily with SOF_2 yielding fluorosilanes and difluorosilanes respectively, but there is no reaction of the Si-O-Si bridge of hexamethyldisiloxane with SOF_2. Very recently it has been shown that SF_4 reacts with trimethylphenoxysilane to yield $PhOSF_3$, $(PhO)_2SF_2$, $(PhO)_3SF$ and $(PhO)_4S$.[143]

The reactions of fluorophosphoranes with disiloxanes and trialkylalkoxysilanes were originally studied with a view to preparing pentacoordinate compounds of the type RPF_3OR''.[183] The following types of reaction were observed:

$$RPF_4 + R'_3SiOSiR'_3 \longrightarrow RPOF_2 + 2R'_3SiF$$

$$RPF_4 + R'_3SiOR'' \longrightarrow RPOF_2 + R'_3SiF + R''F.$$

It is suggested that the instability of the pentacoordinate compounds and the formation of the tetracoordinate compounds $RPOF_2$ is associated with the stability of the strongly polar phosphoryl group. More recent reports[184] show that the reaction of fluorophosphoranes with trimethylphenoxysilane provides a route to stable fluorophosphoranes containing an aryloxy group:

e.g. $Ph_2PF_3 + Me_3SiOPh \longrightarrow Ph_2PF_2OPh + Me_3SiF$.

The interaction of tungsten hexafluoride with alkoxysilanes and hexamethyldisiloxane has recently been studied.[37] The Si-O bonds in hexamethyldisiloxane, trimethylmethoxysilane and dimethylmethoxysilane are cleaved by WF_6 at 0^o to yield the corresponding alkylfluorosilane. There is no evidence for the cleavage of the C-O bond in Me_3SiOMe and $Me_2SiHOMe$, but the Si-H bond is attacked to a small extent. None of the tungsten containing products were characterised, brown or black intractable solids being obtained. The reactions of WF_6 with $(Me_3Si)_2O$ and Me_3SiOMe were carried out with several different ratios of reactants, and the amount of Me_3SiF formed in each case was accurately measured. From this data it is suggested that the main overall reaction between WF_6 and $(Me_3Si)_2O$ is:

$$2(Me_3Si)_2O + WF_6 \longrightarrow 4Me_3SiF + WO_2F_2$$

Additional amounts of Me_3SiF formed in some reactions are accounted for by the slow reaction:

$$(Me_3Si)_2O + WO_2F_2 \longrightarrow 2Me_3SiF + WO_3$$

In reactions with Me_3SiOMe up to four, but not necessarily all four, fluorine atoms of WF_6 are replaced.

The isolation of alkoxy and phenoxy tungsten(VI) fluorides from the reactions of WF_6 with sulphite esters (chapter 2) prompted an investigation of the reactions of WF_6 with alkylalkoxysilanes and trimethylphenoxysilane as routes to the hitherto unreported alkoxy and phenoxy tungsten(VI) fluorides. The formation of tungsten oxotetrafluoride complexes in the reactions of WF_6 with dialkyl ethers (chapter 1) led to a reinvestigation of the reaction of WF_6 with $(Me_3Si)_2O$ as a possible route to WOF_4 and WO_2F_2 and their complexes. This was of particular interest in that the chemical behaviour of WO_2F_2 has not been investigated.[5] The cleavage of the Si-Cl bond in Me_3SiCl by WF_6 to yield WCl_6 and Me_3SiF has been reported,[39] and it was hoped that the interaction of WF_6 with dimethylaminotrimethylsilane would provide a route to dimethylamino derivatives of WF_6.

There have been few reports of fluorine derivatives of transition metal alkoxides. Some alkoxy titanium(IV) fluorides (R = Et, ^nBu) have been reported briefly;[170, 185] the preparation and properties of the series of ethoxy niobium(V) and tantalum(V) fluorides have been described;[171, 186, 187] and some methoxy platinum(~~VI~~ IV) fluorides have recently been obtained.[188] A number of alkoxy tungsten(V)

chlorides[189] and phenoxy tungsten(VI) chlorides[153] have been described.

This chapter describes the reactions of WF_6 with dimethyldimethoxysilane, methyltrimethoxysilane, trimethylphenoxysilane, hexamethyldisiloxane and dimethylaminosilane. These reagents were chosen because of their ready availability or ease of preparation.

The Reactions of Tungsten Hexafluoride with Methylalkoxysilanes and Trimethylphenoxysilane

WF_6 reacts smoothly with methylalkoxysilanes and trimethylphenoxysilane at 20° or below with cleavage of the silicon-oxygen bonds. The products are the corresponding methylfluorosilanes and alkoxy- or phenoxy- tungsten(VI) fluorides. Up to four, but not necessarily all four, fluorine atoms of WF_6 are replaced, in accord with previous observations.[37] The reactions are summarised in Table 3.1, and are described by equations 3.1 to 3.9:

$$2WF_6 + Me_2Si(OMe)_2 \longrightarrow 2WF_5OMe + Me_2SiF_2 \quad (3.1)$$

$$WF_6 + Me_2Si(OMe)_2 \longrightarrow WF_4(OMe)_2 + Me_2SiF_2 \quad (3.2)$$

$$2WF_6 + 3Me_2Si(OMe)_2 \longrightarrow 2WF_3(OMe)_3 + 3Me_2SiF_2 \quad (3.3)$$

$$WF_6 + 2Me_2Si(OMe)_2 \longrightarrow WF_2(OMe)_4 + 2Me_2SiF_2 \quad (3.4)$$

$$WF_6 + MeSi(OMe)_3 \longrightarrow WF_3(OMe)_3 + MeSiF_3 \quad (3.5)$$

$$3WF_6 + 4MeSi(OMe)_3 \longrightarrow 3WF_2(OMe)_4 + 4MeSiF_3 \quad (3.6)$$

$$WF_6 + Me_2Si(OEt)_2 \longrightarrow WF_4(OEt)_2 + Me_2SiF_2 \quad (3.7)$$

$$WF_6 + Me_3SiOPh \longrightarrow WF_5OPh + Me_3SiF \quad (3.8)$$

$$WF_6 + 2Me_3SiOPh \longrightarrow WF_4(OPh)_2 + 2Me_3SiF \quad (3.9)$$

TABLE 3.1

Reactions of tungsten hexafluoride with methylalkoxy(phenoxy)silanes

Reactants (mmoles)	Reaction conditions	Products identified (mmoles)	
WF_6 (19.5) + $Me_2Si(OMe)_2$ (8.3)	0°; 2 hours	Me_2SiF_2[b] WF_5OMe[c] $WF_4(OMe)_2$[c]	Unreacted WF_6 recovered. Ratio WF_5OMe:$WF_4(OMe)_2$ ≃ 2:1[a]
WF_6 (18.0) + $Me_2Si(OMe)_2$ (19.0)	0°; 2 hours	Me_2SiF_2 (18.0)[d] $WF_4(OMe)_2$[e] $WF_3(OMe)_3$[c]	Ratio $WF_4(OMe)_2$:$WF_3(OMe)_3$ 8:1[a]
WF_6 (6.1) + $Me_2Si(OMe)_2$ (16.0)	0°; 8 hours	Me_2SiF_2 (12.1)[d] $WF_2(OMe)_4$[c]	Unreacted $Me_2Si(OMe)_2$(3.3) recovered
WF_6 (11.0) + $MeSi(OMe)_3$ (12.5)	0°; 2 hours	$MeSiF_3$ (12.5)[d] $WF_3(OMe)_3$[e] $WF_2(OMe)_4$[c]	Ratio $WF_3(OMe)_3$:$WF_2(OMe)_4$ ≃ 4:1[a]
WF_6 (14.0) + $MeSi(OMe)_3$ (27.0)	0°; 5 hours	$MeSiF_3$[c,f] $WF_2(OMe)_4$[e]	unreacted $MeSi(OMe)_3$ (8.1) recovered
WF_6 (14.0) + $Me_2Si(OEt)_2$ (13.0)	-80°; 2 hours	Me_2SiF_2 (11.0)[d] $WF_4(OEt)_2$[c,g]	

/contd.

WF_6 (12.5) + Me_3SiOPh (12.5)	20°; 6 hours	Me_3SiF[b] WF_5OPh[c]
WF_6 (8.4) + Me_3SiOPh (18.6)	20°; 12 hours	Me_3SiF (18.0)[b] $WF_4(OPh)_2$[e] $WF_3(OPh)_3$?[h]
WF_6 (7.7) + Me_3SiOPh (22.0)	20°; 2 hours	Me_3SiF (9.5)[d] WF_5OPh[c] $WF_4(OPh)_2$[c]

[a] Ratios determined from the ^{19}F n.m.r. spectra and are very approximate. [b] Identified by i.r. [c] Identified by ^{19}F n.m.r. [d] Identified by i.r. and molecular weight. [e] Identified by analysis and ^{19}F n.m.r. [f] Weak signal due to $MeSi(OMe)F_2$ or $MeSi(OMe)_2F$ present in ^{19}F n.m.r. spectrum. [g] Decomposes rapidly at 20°. [h] Identification based on assignment of single line ^{19}F n.m.r. resonance.

Tetrafluorodimethoxotungsten(VI), $WF_4(OMe)_2$, is a liquid, m.p. ca. 10^o; the other alkoxy and phenoxy tungsten(VI) fluorides are solids at ambient temperatures. The methoxy derivatives are colourless; the phenoxy derivatives are dark red. Apart from WF_5OMe and WF_5OPh, these compounds are involatile at 20^o. The product from the reaction of WF_6 with $Me_2Si(OEt)_2$ is a pale yellow liquid which decomposes at 20^o. Its ^{19}F n.m.r. spectrum is almost identical with that of cis-$WF_4(OMe)_2$, and it is formulated as cis-$WF_4(OEt)_2$. The decomposition of this compound is not as rapid as WF_5OEt (chapter 2).

The alkoxy- and phenoxy- tungsten(VI) fluorides have been characterised by ^{19}F n.m.r. spectroscopy (Table 3.2 gives average values of the spectral parameters), and elemental analyses have been obtained in most cases. The ^{19}F resonances of these compounds occur to higher fields of WF_6 with increasing substitution of F by OR groups, and the simplest interpretation of the spectra is that the compounds are monomeric (as liquids or in solution as appropriate), with octahedral coordination about tungsten as previously suggested for WF_5OMe and WF_5OPh (chapter 2). Molecular weight determinations were not performed because of the hygroscopic nature of the compounds, and the assigned structures are not unambiguous in every case.

In the series of monomeric, octahedral compounds $WF_{6-n}(OR)_n$, geometrical isomerism is possible where n = 2, 3 and 4. The possible geometrical isomers of $WF_4(OR)_2$, $WF_3(OR)_3$ and $WF_2(OR)_4$ are shown in

TABLE 3.2

N.m.r. spectra of $WF_{6-n}(OR)_n$

Compound	Solvent	$^{\delta}$F p.p.m. F_1[c]	F_2[c]	^{1}H Chemical Shift[b] τ	J_{FF} Hz	J_{WF} Hz	J_{HF} Hz	$J(FF)/\nu_o$ [δ]
WF_5OMe	C_6F_6	-118.5	-89.5	4.40	66	43(F_1) 33(F_2)	1(F_1)	0.040
cis-$WF_4(OMe)_2$	neat	-63.5	-44.0	4.65	66	46(F_1) 25(F_2)	1	0.060
trans-$WF_3(OMe)_3$	C_6F_6	-37.0	-13.0	5.00	62		1	0.046
cis-$WF_3(OMe)_3$	C_6F_6		-18.5	4.88		18[d]	1	
trans-$WF_2(OMe)_4$	C_6F_6	+16.0		~5.3		14[d]		
cis-$WF_2(OMe)_4$	C_6F_6		+39.5	~5.3				
cis-$WF_4(OEt)_2$	neat	-60.5	-44.5	4.32 (CH_2) 8.48 (CH_3)	68			0.075
WF_5OPh	C_6F_6	-126.5	-112.0	2.5	65	39(F_1)		0.079
cis-$WF_4(OPh)_2$	CH_3CN	-84.0	-76.0	2.65	68			0.15
cis-$WF_3(OPh)_3$[e]	CH_3CN		-52.5					

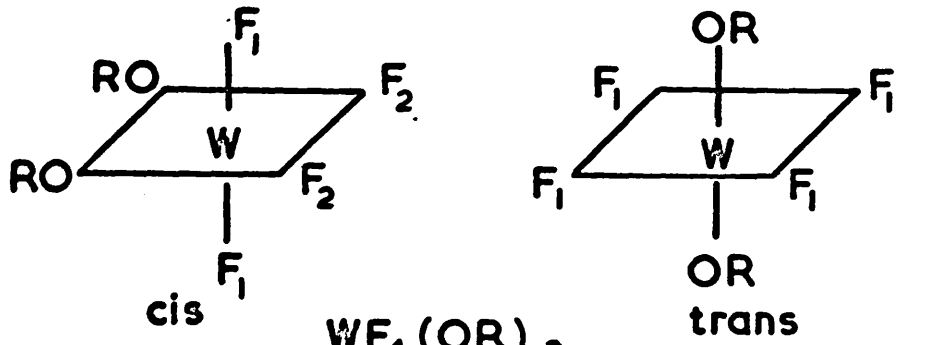
[a] From internal CCl_3F. [b] Mid-points of complex signals (See Text). [c] F_1 trans to F_1, F_2 trans to OR assuming monomeric structure. [d] Incompletely resolved. [e] Tentative assignment.

Figure 3.1. Since octahedral structures are stereochemically rigid in the context of virtually all experimental observations,[75] these isomers will have characteristic ^{19}F n.m.r. spectra, provided that intermolecular exchange processes do not occur. For the compounds $WF_{6-n}(OR)_n$, n = 1-5, R = Me, Et or Ph, the expected ^{19}F n.m.r. spectra, assuming that spin-spin coupling between the fluorine nuclei and the protons of the OR groups is small and does not significantly affect the spectra, are:

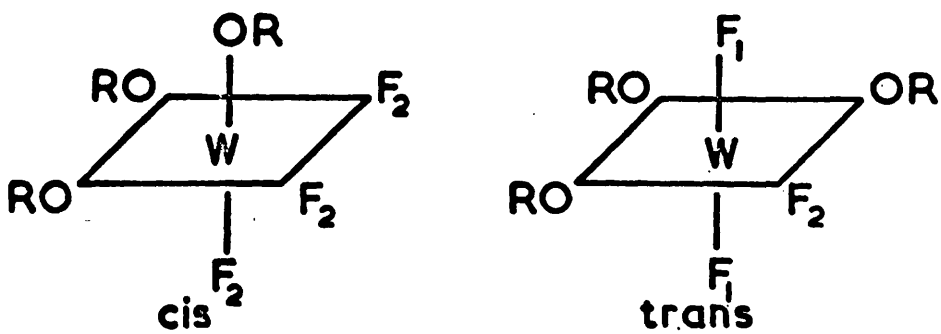
WF_5OR	-	AX_4 or AB_4
cis-$WF_4(OR)_2$	-	A_2X_2 or A_2B_2
trans-$WF_4(OR)_2$	-	single line
cis-$WF_3(OR)_3$	-	single line
trans-$WF_3(OR)_3$	-	AX_2 or AB_2
cis-$WF_2(OR)_4$	-	single line
trans-$WF_2(OR)_4$	-	single line
$WF(OR)_5$	-	single line

The observed ^{19}F n.m.r. spectra are consistent with the above predictions for monomeric octahedral compounds. Figures 3.2 and 3.3 provide examples of the observed spectra of $WF_4(OMe)_2$ and $WF_3(OMe)_3$ and these agree with the calculated A_2B_2 and AB_2 spectra for the similar values of $J/\nu_o\delta$ (Figures 3.4 and 3.5). Coupling between

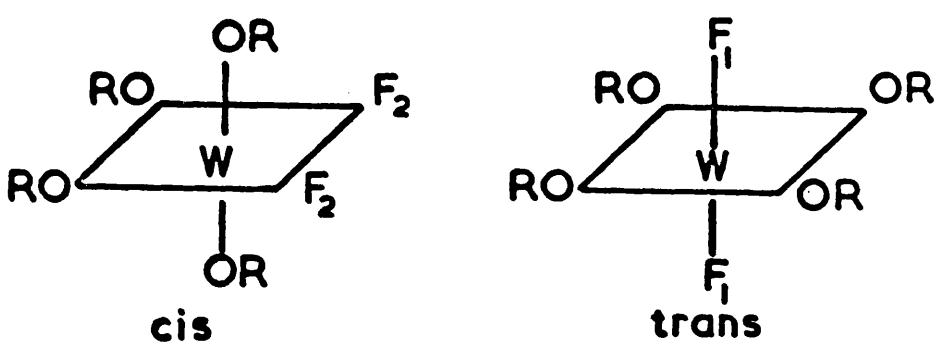
Geometrical Isomerism in $WF_{6-n}(OR)_n$



$WF_4(OR)_2$



$WF_3(OR)_3$



$WF_2(OR)_4$

Figure 3.1

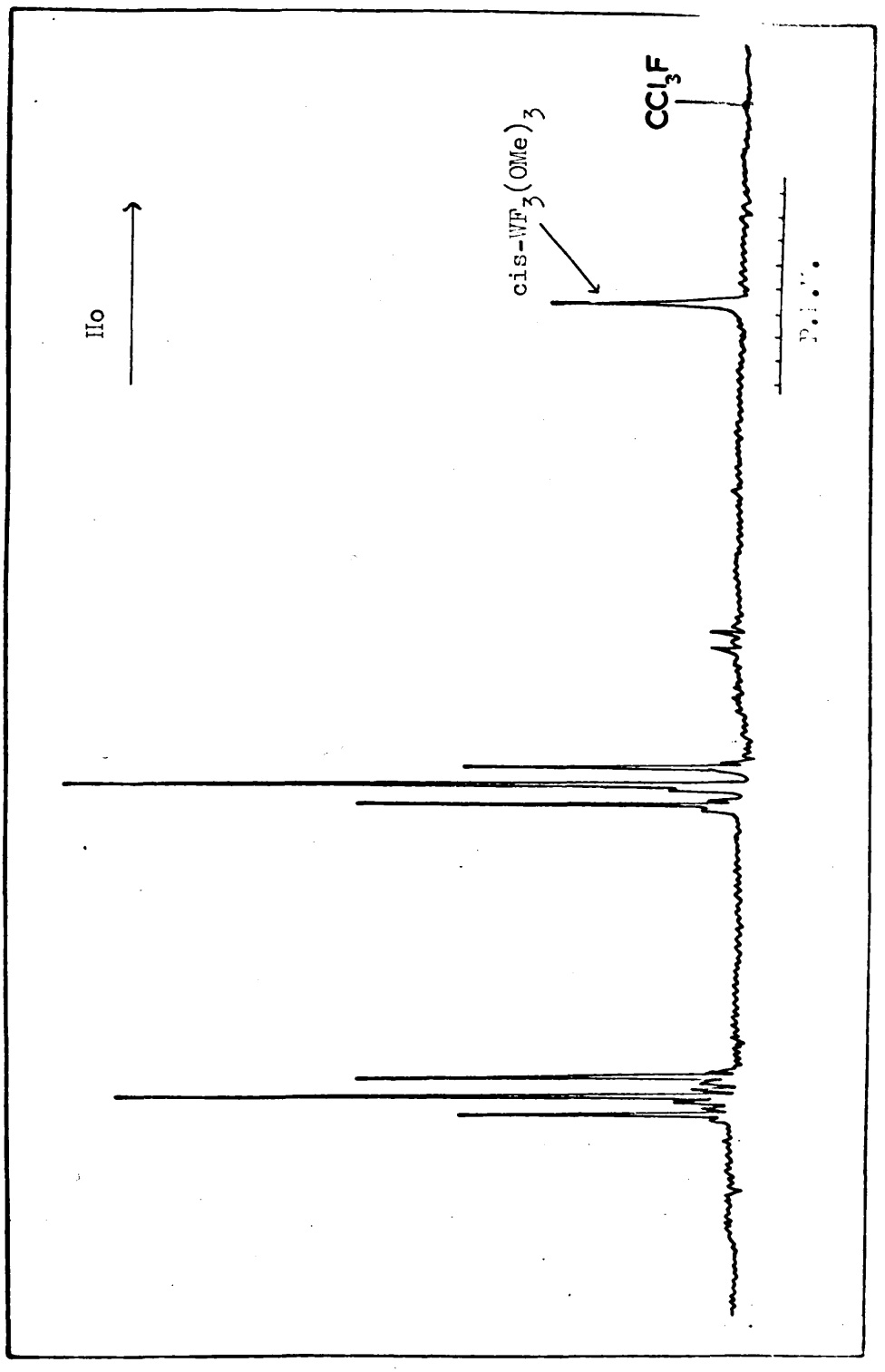


FIGURE 3.2: ^{19}F n.m.r. spectrum of neat $WF_4(OMe)_2$

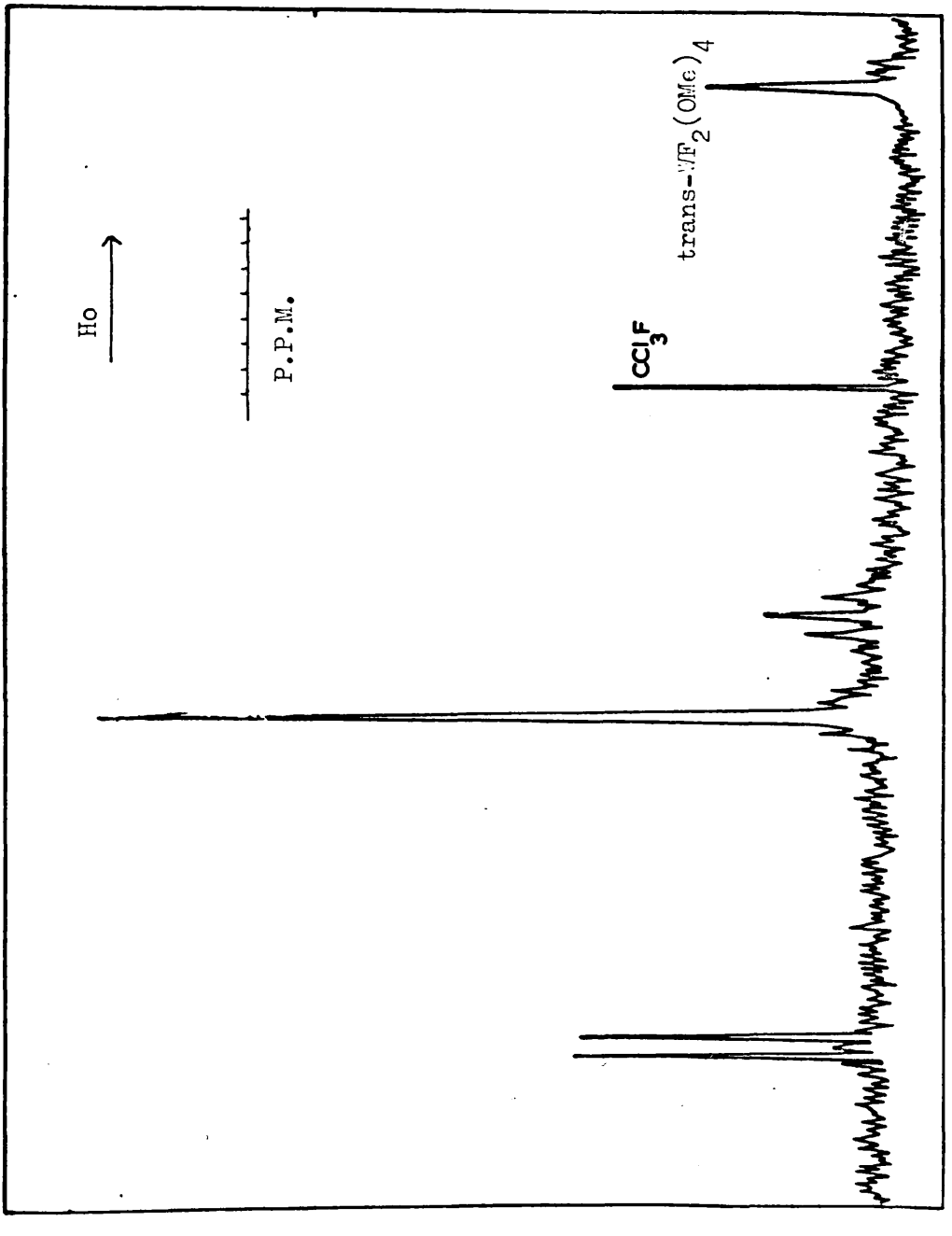
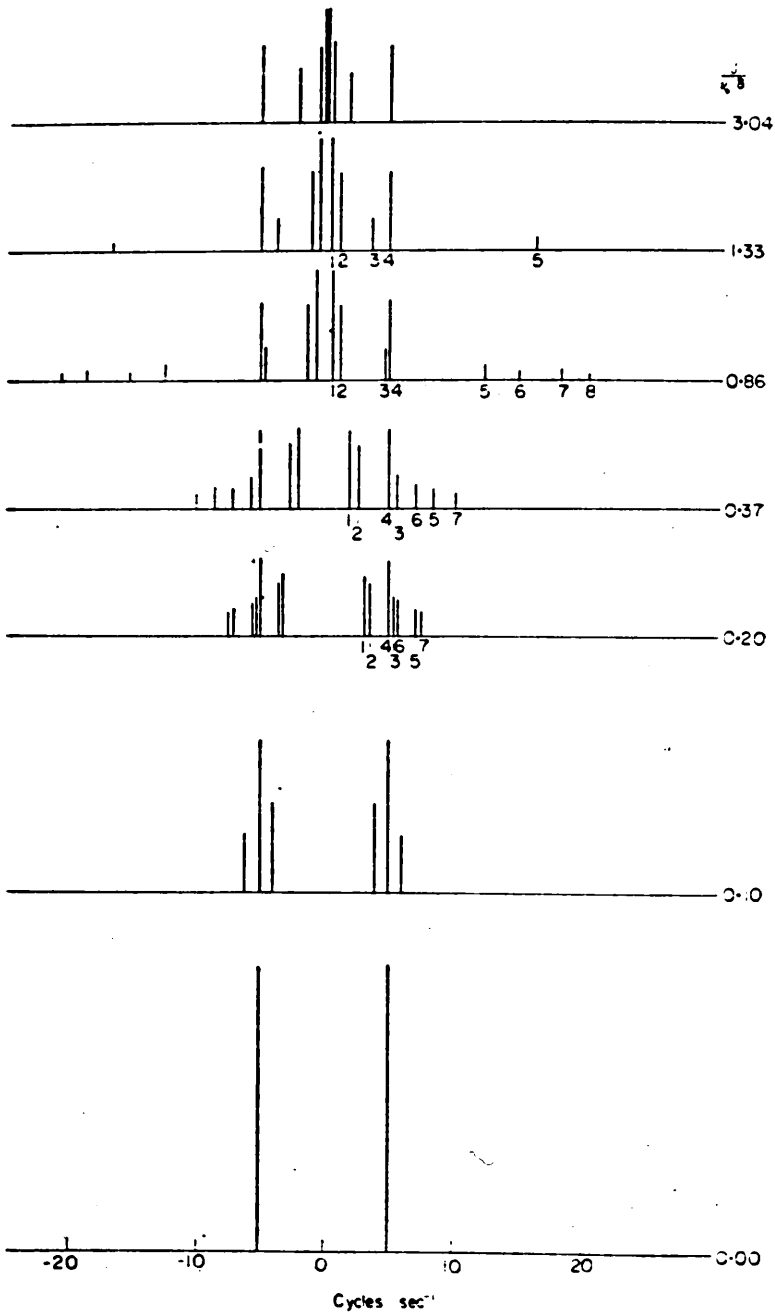
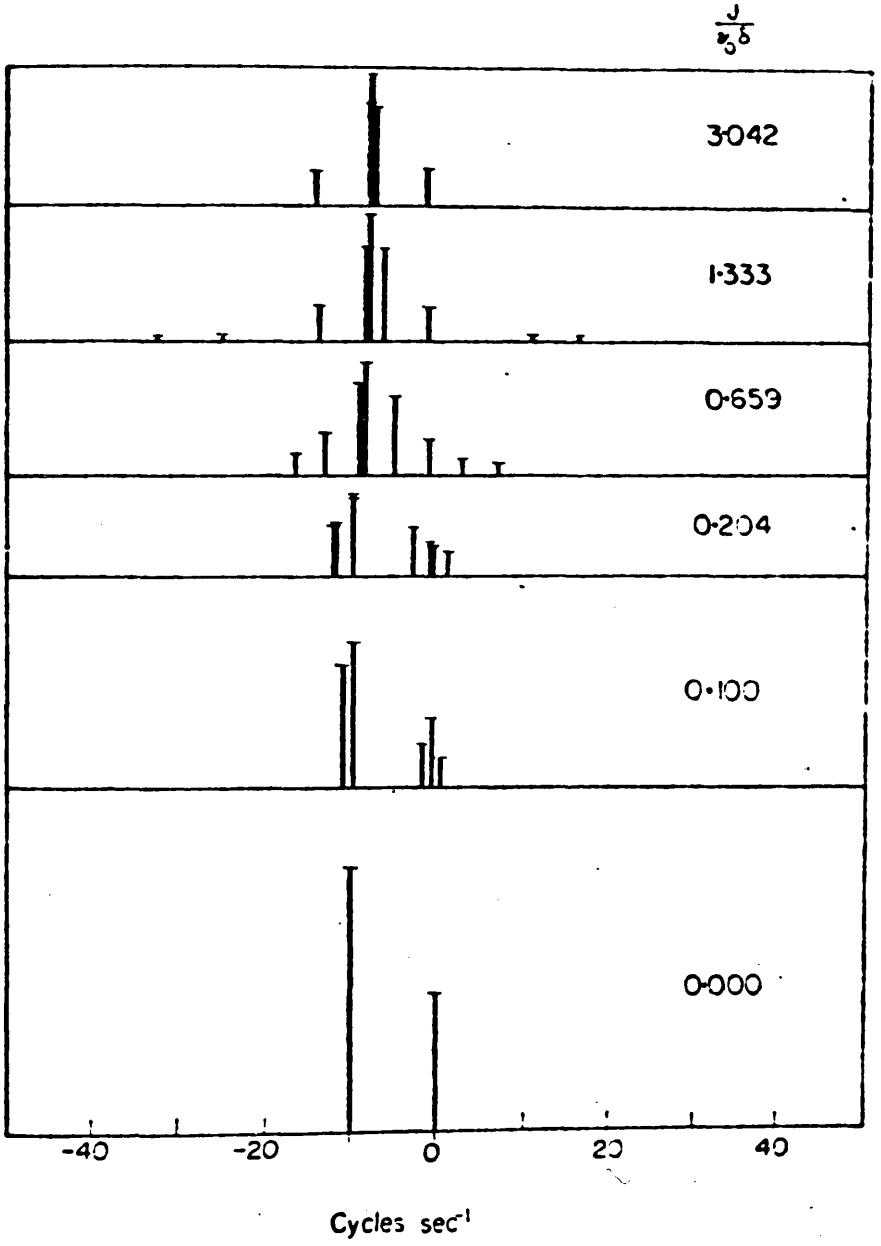


FIGURE 3.3: ^{19}F n.m.r. spectrum of $WF_3(OMe)_3$ in C_6F_6



A_2B_2 type theoretical spectra for a chemical shift difference ($\nu_0\delta$) of 10 cycles sec $^{-1}$.

Figure 3.4 (ref. 141)



AB_2 theoretical spectra for nuclei of spin $\frac{1}{2}$ and a chemical shift difference $\nu_0\delta$ of 10 cycles sec^{-1}

Figure 3.5 (ref. 141)

the protons of the OR groups and the fluorine atoms in $WF_{6-n}(OR)_n$ is of the order of 1 Hz, and does not significantly affect the first-order structure of the ^{19}F n.m.r. spectra.

In the alkoxy- and phenoxy- tungsten(VI) fluorides there are two possible environments for the fluorine atoms, viz trans to another fluorine (F_1), and trans to an OR group (F_2). In WF_5OMe, WF_5OPh and trans-$WF_3(OMe)_3$ there are unequal numbers of fluorine atoms in two environments, giving rise to AB_4 and AB_2 spectra respectively, and assignment of the ^{19}F resonances can be made with complete certainty. F_1 nuclei resonate to lower field of F_2 nuclei. In cis-$WF_4(OR)_2$ (R = Me, Et, Ph) there are equal numbers of fluorine atoms in two environments, giving rise to A_2B_2 spectra, and assignments of the resonances cannot be made with complete certainty. It is assumed in this case that the F_1 nuclei resonate at lower field than the F_2 nuclei.

Assignments of single line ^{19}F n.m.r. spectra are much less certain, as the possibility of spectroscopic equivalance of ^{19}F nuclei arising from fast exchange processes in polymeric structures cannot be eliminated. Both isomers of $WF_2(OMe)_4$ give single lines, and the resonance at lower field is assigned to the trans isomer (F_1 nuclei). There are no resonances which can be assigned to trans $WF_4(OR)_2$ species.

It has recently been shown[190] that the chemical shifts of the

^{19}F nuclei in substituted hexafluorostannates of the type $[SnF_{6-n}X_n]^{2-}$, relative to SnF_6^{2-}, are given to a good approximation by $\delta = pC + qT$, where C and T are constants characteristic of the ligand X, and p and q are the numbers of substituents cis and trans to the fluorine atoms respectively. This empirical relationship can be applied with equal success to compounds in the series $WF_{6-n}(OR)_n$, and lends some weight to the assignments given above. Table 3.3 lists the observed and calculated values of the ^{19}F chemical shifts using C = 43.5, T = 74.3 for R = Me, and C = 36.0, T = 55.0 for R = Ph. The agreement is not perfect, but no correction has been made for solvent effects. These are considerable, and, for example, there is 9 p.p.m. difference between the ^{19}F chemical shift of cis-$WF_3(OMe)_3$ in $WF_4(OMe)_2$ and in C_6F_6. The average discrepancy between calculated and observed ^{19}F chemical shifts is 6.2 p.p.m. for R = Me (9 values over 138 p.p.m.) and 6.0 p.p.m. for R = Ph (5 values over 64 p.p.m.).

The ^1H n.m.r. spectra of the methoxy tungsten(VI) fluorides are reproducible, but are not first-order. The resonances from non-equivalent OR groups are not resolved, and the values of the ^1H chemical shifts in Table 3.2 are the mid-points of complex multiplets. The ^1H n.m.r. signals are found at higher fields with increasing substitution by OMe groups. In all cases except $WF_2(OMe)_4$ assignment of the ^1H n.m.r. signals to a particular isomer is possible by comparison of the relative intensities with those of the ^{19}F n.m.r.

TABLE 3.3

Comparison of experimental with calculated ^{19}F chemical shifts.

Compound	Experimental chemical shifts (p.p.m.)[a] F_1	F_2	Calculated chemical shifts (p.p.m.)[b] F_1	F_2
WF_5OMe	46	75	44	74
cis-$WF_4(OMe)_2$	101	121	87	118
trans-$WF_3(OMe)_3$	128	152	131	161
cis-$WF_3(OMe)_3$		146		161
cis-$WF_2(OMe)_4$		204		205
trans-$WF_2(OMe)_4$	182		175	
WF_5OPh	39	53	36	55
cis-$WF_4(OPh)_2$	81	89	72	91
cis-$WF_3(OPh)_3$		113		127

[a] From WF_6, using the relationship $\delta_{WF_6} = \delta_{CCl_3F} + 165$ p.p.m. [b] Using $\delta(F) = pC + qT$ and C = 43.5, T = 74.3 for OMe and C = 36.0, T = 55.0 for OPh.

signals. The ^{1}H n.m.r. spectrum of $WF_2(OMe)_4$ consists of 4 groups of signals, a triplet, a doublet, a single line and a doublet, with relative intensities 5:2:3:5 which do not agree with those of the ^{19}F n.m.r. signals. The possibility of the presence of another compound containing OMe but not fluorine cannot be excluded.

The Reactions of Tungsten Hexafluoride with Hexamethyldisiloxane and Dimethylaminotrimethylsilane

A slow reaction occurs between WF_6 and hexamethyldisiloxane at 20° to yield WOF_4 (10% yield) and trimethylfluorosilane:

$$(Me_3Si)_2O + WF_6 \longrightarrow 2Me_3SiF + WOF_4 . \qquad (3.10)$$

There is no evidence for the formation of WO_2F_2 as previously suggested,[37] but some reduction of WF_6 also occurs.

The reaction between WF_6 and dimethylaminotrimethylsilane is vigorous at low temperatures, and trimethylfluorosilane is formed. The tungsten-containing product is a brown oil which has not been characterised.

The Thermal Decomposition of Alkoxy Tungsten(VI) Fluorides

It has been shown previously (chapter 2) that thermal decomposition of WF_5OMe yields WOF_4 and methyl fluoride, and that WF_5OPh is stable up to 180°. Thermal decomposition of $WF_{6-n}(OMe)_n$ at 80° (n = 2), 100° (n = 3) and 145° (n = 4) yields dimethyl ether and small amounts of methyl fluoride (n = 3, 4). Some reduction of the tungsten occurs in each case. The thermal decomposition of

$WF_4(OMe)_2$ at 80° yields $WOF_4.OMe_2$ (40%), and isomerisation of cis-$WF_4(OMe)_2$ to $WOF_4.OMe_2$ occurs slowly at ambient temperatures. Thermal decomposition of $WF_2(OMe)_4$ at 145° yields a blue solid with a W:F ratio of 1.5:1. Thermal decomposition of the unstable compound $WF_4(OEt)_2$ at 50° does not yield $WOF_4.OEt_2$.

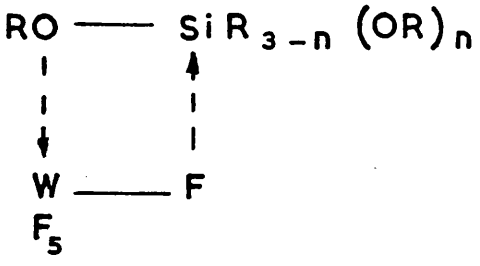
Discussion

In the reactions of WF_6 with methylalkoxysilanes and trimethylphenoxysilane, successive replacement of up to four fluorine atoms of WF_6 by alkoxyl groups occurs. Although substitution beyond four (OMe) or three (OPh) was not observed, there appears to be no reason why the remaining members of the series should not be stable as $W(OPh)_6$ is known.[153] In each of the reactions in Table 3.1 the expected products are obtained, except in one case where the ratio of reactants WF_6:$Me_2Si(OMe)_2$ is >2:1. The presence of cis-$WF_4(OMe)_2$ in the products of this latter reaction in addition to the expected WF_5OMe suggests that cis-$WF_4(OMe)_2$ is readily formed, and that the reverse reaction,

$$WF_6 + WF_4(OMe)_2 \not\longrightarrow 2WF_5OMe \quad ,$$

does not occur at the temperature of the reaction (0°). Consistent with the ready formation of cis-$WF_4(OMe)_2$ is the observation that WF_5OMe is not present in the products of the reaction of WF_6 (1 mole) with $Me_2Si(OMe)_2$ (2 mole) after 30 minutes, while cis-$WF_4(OMe)_2$ and higher substituted products are present.

It has been proposed[180, 191] that cleavage of silicon-oxygen bonds by Lewis acids proceeds via a weak four-centre transition state. For the reactions involving WF_6 the following transition state can be visualised:



The ability of WF_6 to form such weak donor-acceptor complexes is well established (chapter 1), and the difference in Si-F and Si-O bond energy terms (e.g. D(Si-F) in SiF_4 = 135 kcal/mole; D(Si-O) in silica = 108 kcal/mole[167]) contributes to the thermodynamic feasibility of the reactions. The rate of substitution of the fluorine atoms of WF_6 by OR groups appears to decrease with increasing numbers of OR groups bound to tungsten, and to be faster for OMe than for OPh. There is, however, no direct evidence, e.g. kinetic data, for this.

The cleavage of the Si-O-Si bridge in hexamethyldisiloxane by

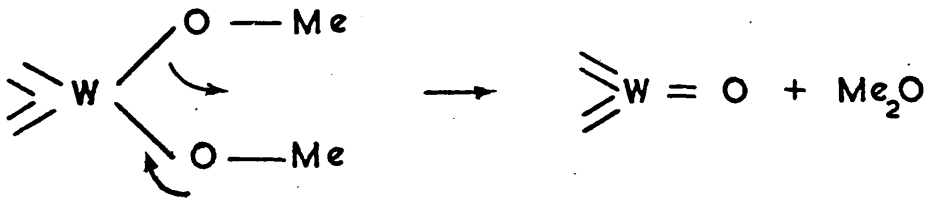
WF_6 may proceed by a pathway similar to that proposed for the cleavage of dialkyl ethers by WF_6 (chapter 1):

$$WF_6 + (Me_3Si)_2O \longrightarrow [F_6W.O(SiMe_3)_2] \rightarrow [WF_5OSiMe_3] + Me_3SiF$$
$$\longrightarrow WOF_4 + 2Me_3SiF$$

Siloxanes are much weaker donors than dialkyl ethers, and this has been explained on the basis of oxygen-to-silicon $p\pi - d\pi$ bonding in the former.[192] This may account in part for the slow reaction between WF_6 and $(Me_3Si)_2O$, and preclude the formation of a WOF_4 - $(Me_3Si)_2O$ complex. Alkoxysilanes should be stronger donors than siloxanes as there is only one silicon atom to encourage oxygen-to-silicon π-bonding,[193] and it is interesting that the reactions of WF_6 with alkoxysilanes are much more rapid than with hexamethyldisiloxane.

The failure of Viswanathan and Van Dyke[37] to isolate the alkoxy tungsten(VI) fluorides described here from the reaction of WF_6 with trimethylmethoxysilane is not understood. Incomplete removal of water from their reaction systems may have caused extensive hydrolysis of the tungsten-containing products. It is also possible that Me_3SiOMe behaves as a reducing agent towards WF_6.

The mechanisms of the thermal decompositions of methoxy tungsten(VI) fluorides probably involve the initial formation of a stable W=O bond, with the elimination of Me^+ (cf. behaviour of WF_5OMe, chapter 2), and the subsequent formation of dimethyl ether:



Buslaev and co-workers have shown that niobium(V) and tantalum(V) alkoxyfluorides react with ionic fluorides to yield oxo-compounds with the elimination of the corresponding dialkyl ether, and a mechanism involving alkyl cations is proposed.[186] The study of the mechanisms of the thermal decompositions of methoxy tungsten(VI) fluorides, possibly by ^{18}F tracer studies, affords scope for future work. It was hoped that the thermal decompositions of cis-$WF_4(OEt)_2$ and $WF_2(OMe)_4$ would yield $WOF_4.OEt_2$ and WO_2F_2 respectively. If WO_2F_2 is formed in the latter case, it may be reduced under the conditions of the reaction.

WF_6 readily cleaves the Si-N bond in Me_3SiNMe_2, but the failure to isolate dimethylamino derivatives of WF_6 is not understood, especially in light of the recent report of the preparation of $W(NMe_2)_6$.[194] Further work on the control of reaction conditions is necessary.

The ^{19}F n.m.r. spectra and the preferred stereochemistries of $WF_{6-n}(OR)_n$ compounds are discussed in chapter 4.

Conclusions

The fluorination of methylalkoxysilanes and trimethylphenoxysilane with WF_6 provides a route to the compounds $WF_{6-n}(OR)_n$, n = 1-4(Me), n = 1,2(Ph). Future work might be directed towards the preparation of the remaining members of these series. The simplest interpretation of the ^{19}F n.m.r. spectra of these compounds is that they have monomeric, octahedral structures, displaying geometrical isomerism in some cases. The ^{19}F resonances are all to high field of WF_6, and the effects of OMe and OPh substituents on the chemical shifts are approximately additive.

$WF_4(OMe)_2$ isomerises to $WOF_4.OMe_2$, and thermal decompositions of $WF_3(OMe)_3$ and $WF_2(OMe)_4$ yield Me_2O and MeF. Further work on the control of these decompositions is necessary as they may provide routes to other oxofluoro-complexes of tungsten.

The data for the reactions of WF_6 with hexamethyldisiloxane and dimethylaminotrimethylsilane are incomplete, but establish that Si-O and Si-N bond cleavage occurs. In the former case WOF_4 is obtained in low yield.

EXPERIMENTAL SECTION

Chemicals

Dimethyldimethoxysilane, methyltrimethoxysilane, hexamethyldisiloxane, dimethylaminotrimethylsilane (Aldrich), and trimethylphenoxysilane (prepared from Me_3SiCl and PhOH,[195]) were dried over activated Linde 4A molecular sieves and degassed before use. WF_6 and solvents were purified as described previously (chapters 1, 2).

Experimental procedure

Reactions were carried out in a high-vacuum system, and rigorous precautions were taken to exclude moisture. Reactants were condensed together into glass reaction vessels cooled in liquid nitrogen, and allowed to warm slowly until reaction occurred. Involatile products were handled in a dry-box. A description of the reaction vessels and instrumentation is given in the Appendix.

Reactions of tungsten hexafluoride.

The conditions and products of the reactions of WF_6 with the methylalkoxysilanes and with trimethylphenoxysilane are summarised in Table 3.1. The n.m.r. spectra of $WF_{6-n}(OR)_n$ compounds (R= Me,Et,Ph) are summarised in Table 3.2. The ^{19}F n.m.r. signals of $WF_{6-n}(OR)_n$ showed complex splittings from ^1H - ^{19}F spin-spin coupling ($J \sim 1$ Hz),

but these were only resolved on maximum scale expansion, and are not included in descriptions of the ^{19}F n.m.r. spectra given in subsequent sections.

(1) Tungsten hexafluoride and dimethyldimethoxysilane

(a) WF_6 (5.8 g, 19.5 mmoles) and $Me_2Si(OMe)_2$ (1.0 g, 8.3 mmoles) gave a yellow solution at -80°. Reaction occurred slowly at this temperature, and became vigorous as the temperature was raised to 0°. The reaction was complete in 2 hours, yielding a white solid and a colourless supernatant liquid. The latter was volatile at -80°, and was identified from its infrared spectrum as a mixture of dimethyldifluorosilane[196] and WF_6.[101] Separation of these compounds was not attempted.

The ^{19}F n.m.r. spectrum of the solid product in C_6F_6 (CCl_3F ref.) contained signals at -116.9 p.p.m. (doublet, J_{FF} = 67 Hz, J_{WF} = 45 Hz) and -80.4 p.p.m. (quintet, J_{FF} = 67 Hz) with relative intensities 4:1, characteristic of pentafluoromethoxotungsten(VI), (Table 2.3), and signals of equal intensity at -64.0 p.p.m. and -46.0 p.p.m. (triplets, J_{FF}=67 Hz), characteristic of cis-tetrafluorodimethoxotungsten(VI) $WF_4(OMe)_2$ (cf.1b below). From the intensities of the signals the ratio of the products was estimated as WF_5OMe: $WF_4(OMe)_2 \cong 2:1$.

(b) WF_6 (5.3 g, 18 mmoles) and $Me_2Si(OMe)_2$ (2.3 g, 19 mmoles) reacted at 0° (2 hours) to give two colourless immiscible liquids. The

fraction volatile at -20° was identified from its infrared spectrum[196] and molecular weight as dimethyldifluorosilane (1.7 g, 18 mmoles).

Molecular weight: found, 96.7; Me_2SiF_2 requires, 96.2.

A colourless, viscous liquid (5.9 g, m.pt.~10°), involatile at 20°, remained. The ^{19}F n.m.r. spectrum (neat liquid, CCl_3F ref.) contained major signals of equal intensity at -63.5 p.p.m. and -43.9 p.p.m. (triplets, J_{FF} = 67 Hz) assigned to cis-tetrafluoro-dimethoxotungsten(VI), $WF_4(OMe)_2$. Signals of less intensity (9% of total) at -12.8 p.p.m. (single line) and -34.5 p.p.m. (doublet, J_{FF} = 62 Hz) were assigned to cis-and trans-$WF_3(OMe)_3$ respectively (cf. 2a, below). The ^1H n.m.r. spectrum contained a major signal at 4.64 τ (multiplet, minimum of 5 lines, J~1 Hz), and weak multiplets at 4.96 τ and 5.02 τ. Because of the extremely hygroscopic nature of $WF_4(OMe)_2$ and $WF_3(OMe)_3$, separation of the involatile products was not attempted.

Elemental Analysis. Found: C, 8.06; H, 2.07; F, 23.3; W, 56.0%. $C_2H_6F_4O_2W$ requires: C, 7.46; H, 1.88; F, 23.6; W, 57.1%.

(c) WF_6 (1.8 g, 6.1 mmoles) and $Me_2Si(OMe)_2$ (1.9 g, 16 mmoles) reacted at 0° (8 hours) to give a white crystalline solid and a colourless supernatant liquid. The latter was volatile at -40° and was identified from its infrared spectrum[196] and molecular weight as Me_2SiF_2 (1.2 g, 12.1 mmoles).

Molecular weight: found, 96.8; Me_2SiF_2 requires, 96.2.

The fraction volatile at 20° was unreacted $Me_2Si(OMe)_2$ (0.4 g, 3.3 mmoles).

The solid product (2.1 g) was sparingly soluble in C_6F_6. The ^{19}F n.m.r. spectrum (CCl_3F ref.) contained signals at + 16.7 p.p.m. and + 39 p.p.m. (single lines) with relative intensities 3:1, assigned to trans- and cis-difluorotetramethoxotungsten(VI), $WF_2(OMe)_4$, respectively (cf. 2b, below). The ^1H n.m.r. spectrum contained signals at 5.18τ (triplet, J=1.2 Hz), 5.25τ (doublet, J=1.9 Hz), 5.33τ (single line), and 5.45τ (doublet, J=0.7 Hz) with relative intensities 5:2:3:5.

Anal. Found: W, 53.5%. $WF_2(OMe)_4$ requires: W, 53.1%.

(2) Tungsten hexafluoride and methyltrimethoxysilane.

(a) WF_6 (3.3 g, 11 mmoles) and $MeSi(OMe)_3$ (1.7 g, 12.5 mmoles) reacted vigorously at 0°. The reaction was complete after 2 hours, yielding a white solid and a colourless supernatant liquid. The latter was volatile at 25°, and was identified from its infrared spectrum [197] and molecular weight as methyltrifluorosilane (1.3 g, 12.5 mmoles). Molecular weight: found, 100.1; $MeSiF_3$ requires, 100.1.

The residue was a white, involatile solid (3.7 g) whose ^{19}F n.m.r. spectrum in C_6F_6 (CCl_3F ref.) contained a major signal at -18.7 p.p.m. (single line, J_{WF}, partially resolved = 18 Hz) assigned to cis-trifluorotrimethoxotungsten(VI), $WF_3(OMe)_3$; signals at -37.1 p.p.m. (doublet, J_{FF}=62Hz) and -12.9 p.p.m. (triplet, J_{FF} = 62 Hz) with relative intensities 2:1, assigned to trans-trifluorotrimethoxo-

tungsten(VI), $WF_3(OMe)_3$; and a single line (18% of total signal intensity) at + 16.6 p.p.m. assigned to trans-$WF_2(OMe)_4$. The ratio of isomers, cis-$WF_3(OMe)_3$: trans-$WF_3(OMe)_3$ was 2:1. The ^1H n.m.r. spectrum contained major signals at 4.88 τ (multiplet, minimum of 6 lines, J~0.8 Hz) and 5.00τ (multiplet, minimum of 3 lines, J~1 Hz) with relative intensities 2:1, and multiplets of less intensity at 4.72 τ and 5.16τ.

Anal. Found: C, 11.2; H, 2.94; F, 16.1%. $C_3H_9F_3O_3W$ requires: C, 10.8; H, 2.71; F, 17.1%.

(b) WF_6(4.1 g, 14 mmoles) and $MeSi(OMe)_3$ (3.7 g, 27 mmoles) reacted at 0° (5 hours), yielding a white solid and a supernatant colourless liquid. The latter was volatile at -70° (1.7 g) and was identified from its infrared spectrum[197] as $MeSiF_3$.

Molecular weight: found, 102.1. $MeSiF_3$ requires, 100.1. The ^{19}F n.m.r. spectrum of this fraction (CCl_3F ref.) contained a major signal at + 139.7 p.p.m. (quartet, J_{HF} = 4Hz, with satellite peaks, J_{SiF} = 270Hz)characteristic of $MeSiF_3$[197], and a signal of less intensity (7% of total) at + 141.3 p.p.m. (quartet, J = 4 Hz) which may have been due to $MeSiF_2(OMe)$ or $MeSiF(OMe)_2$. The molecular weight of the fraction was consistent with this.

The fraction volatile at 25° was unreacted $MeSi(OMe)_3$ (1.1 g, 8.1 mmoles).

The solid product was identified as difluorotetramethoxo-

tungsten(VI), $WF_2(OMe)_4$ (5.0 g, 14 mmoles).

Anal. Found: C, 14.5; H, 3.68; F, 10.0; W, 53.4%.

$C_4H_{12}F_2O_4W$ requires: C, 13.9; H, 3.50; F, 11.0; W, 53.1%.

The ^{19}F n.m.r. spectrum in C_6F_6 (CCl_3F ref.) contained signals at + 15.1 p.p.m. (single line, J_{WF}, partially resolved, = 14 Hz) and + 40.1 p.p.m. (single line) with relative intensities 3:1 assigned to trans- and cis-$WF_2(OMe)_4$ respectively. The ^1H n.m.r. spectrum contained signals at 5.19 τ (triplet, J=1.3 Hz), 5.26 τ (doublet, J=2 Hz), 5.38 τ (single line) and 5.48 τ (doublet, J = 0.7 Hz), with relative intensities 5:2:3:5.

(3) Tungsten hexafluoride and dimethyldiethoxysilane.

WF_6 (4.2 g, 14 mmoles) and $Me_2Si(OEt)_2$ (1.9 g, 13 mmoles) reacted slowly at -80° (2 hours), yielding a pale yellow liquid.

The fraction volatile at -80° was identified from its infrared spectrum[196] as dimethyldifluorosilane (1.1 g, 11 mmoles).

Molecular weight: found, 97.5; Me_2SiF_2 requires, 96.2.

The other product was a pale-yellow, involatile, viscous liquid, whose ^{19}F n.m.r. spectrum (neat liquid, CCl_3F ref.) contained two triplets of equal intensity (J_{FF} = 68Hz) at -60.6 p.p.m. and -44.4 p.p.m. assigned to cis-tetrafluorodiethoxotungsten(VI), $WF_4(OEt)_2$, and a single line of much less intensity (2% of total) at -63.0 p.p.m. The ^1H n.m.r. spectrum contained major signals at 4.35 τ (broad multiplet, minimum of 4 lines, J=7 Hz) and 8.48 τ (multiplet,

minimum of 6 lines, J=7 Hz) with relative intensities 2:3, and signals of less intensity at 4.62τ (single line), 5.14 τ (quartet, J=7 Hz), 5.94 τ (quartet, J=7 Hz), 8.20 τ (triplet, J=7 Hz) and 9.70 τ (triplet, J=7 Hz). The ^{19}F n.m.r. spectrum was re-run after 1 hour, and consisted of a broad singlet at -66.7 p.p.m.

(4) Tungsten hexafluoride and trimethylphenoxysilane

(a) WF_6 (3.7 g, 12.5 mmoles) and Me_3SiOPh (2.1 g, 12.5 mmoles) reacted vigorously at 20°, yielding a deep red solution. The reaction was complete after 6 hours.

The fraction volatile at -20° was identified from its infrared spectrum as trimethylfluorosilane.[198]

The other product was a dark red crystalline solid, which sublimed slowly at 25°. The ^{19}F n.m.r. spectrum in C_6F_6 (CCl_3F ref.) was characteristic of an AB_4 system, which could be analysed as AX_4 to a first approximation, and contained signals at -126.5 p.p.m. (doublet, J_{FF} = 66Hz, J_{WF} = 38Hz) and -112.1 p.p.m. (multiplet, minimum of 5 lines, J_{FF} = 66Hz), characteristic of pentafluorophenoxotungsten(VI) (Table 2.3).

(b) WF_6 (2.5 g, 8.4 mmoles) and Me_3SiOPh (3.1 g, 18.6 mmoles) reacted at 20° (12 hours) yielding Me_3SiF (1.7 g, 18 mmoles) and a dark red, involatile solid (3.9 g). The latter was sparingly soluble in CH_3CN, and the solutions were too dilute for good resolution of ^1H and ^{19}F n.m.r. spectra. The ^{19}F n.m.r. spectrum

(CCl_3F ref.) was characteristic of an A_2B_2 system, which could be analysed as an A_2X_2 spectrum to a first approximation, and contained signals of equal intensity at -83.8 p.p.m. and -75.8 p.p.m. (triplets, J_{FF} = 68Hz)assigned to cis-tetrafluorodiphenoxotungsten(VI), $WF_4(OPh)_2$. A weak single line in the ^{19}F n.m.r. spectrum at -52.4 p.p.m. (5% of total intensity) was tentatively assigned to cis-trifluorotriphenoxotungsten(VI), $WF_3(OPh)_3$, by analogy with cis-$WF_3(OMe)_3$.

Anal. Found: C, 32.8; H, 2.40; F, 16.0; W, 39.7%.
$C_{12}H_{10}F_4O_2W$ requires: C, 32.3; H, 2.26; F, 17.0; W, 41.2%.
Infrared spectrum (nujol mull, 1200-400 cm^{-1}): 1198m, 1150w, 1064w, 1013w, 935sh, 929m, 904w, 754s, 715w, 671m, 662m, 650s, 618m, 596m cm^{-1}.

(c) WF_6 (2.3 g, 7.7 mmoles) and Me_3SiOPh (3.7 g, 22 mmoles) reacted smoothly at 20° (2 hours).

The fraction volatile at -60° was identified from its infrared spectrum as Me_3SiF[198] (0.9 g, 9.5 mmoles).
Molecular weight: found, 94.1; Me_3SiF requires 92.1.

A dark-red solid remained after removal of all the volatile material, and elemental analysis gave: C, 31.1; H, 2.34; F, 17.5%. $WF_4(OPh)_2$ requires: C, 32.3; H, 2.26; F, 17.0%. This product was sparingly soluble in benzene, and the ^{19}F n.m.r. spectrum (CCl_3F ref.) contained signals at -126.7 p.p.m. (doublet, J_{FF} = 65 Hz) and

-112.0 p.p.m. (multiplet, minimum of 5 lines) characteristic of WF_5OPh (Table 2.3), and a multiplet with a minimum of 9 lines at -86.5 p.p.m., typical of an A_2B_2 system, assigned to cis-$WF_4(OPh)_2$.

(5) Tungsten hexafluoride and hexamethyldisiloxane

WF_6 (3.1 g, 10.5 mmoles) and $(Me_3Si)_2O$ (1.7 g, 10.5 mmoles) were allowed to react at 20°. The mixture was initially deep orange, but darkened after approx. 10 minutes, depositing a black solid. After 24 hours the reaction mixture had separated into two layers; the upper layer was pale yellow, and the lower, blue-black.

The fraction volatile at -80° (2.2 g) was identified from its infrared spectrum as a mixture of Me_3SiF[198] and WF_6,[101] and separation of these was not attempted.

Molecular weight: found, 107.7; Me_3SiF requires, 92.2; WF_6 requires, 297.9.

The fraction volatile at 20° was unreacted $(Me_3Si)_2O$ (0.9 g, 5.5 mmoles).

The involatile product was a dark brown solid (1.7 g), from which a white solid (0.3 g) was sublimed (25°, over 30 hours), and identified as tungsten oxotetrafluoride, WOF_4 (yield 10%). Its infrared spectrum contained absorptions characteristic of WCF_4[50] at 1048s, 730m, 650s cm^{-1}, and additional absorptions at 1242w and 1188s cm^{-1}.

Anal. Found: F, 27.6%. WOF_4 requires: F, 27.5%

(6) Tungsten hexafluoride and dimethylaminotrimethylsilane

WF_6 (2 g, 6.7 mmoles) and Me_3SiNMe_2 (0.6 g, 5 mmoles) were allowed to react at -60°. The mixture was initially bright red. A vigorous reaction occurred after a few minutes, and was complete in 30 minutes.

The fraction volatile at -80° was identified from its infrared spectrum as Me_3SiF[198], but the yield was not measured. The involatile residue was a brown oil which was not investigated.

Thermal decomposition of alkoxytungsten(VI) fluorides

The thermal decompositions were carried out in large glass vessels (volume 200 ml) fitted with teflon stopcocks, and the progress of the decompositions was observed by monitoring changes in pressure. $WF_4(OMe)_2$, $WF_3(OMe)_3$ and $WF_2(OMe)_4$ were prepared in situ from WF_6 and the appropriate alkylalkoxysilane. Small quantities of other members of the series may have been present in each case. Careful regulation of the temperature of the decomposition was necessary as explosions occurred in some experiments.

(1) Tetrafluorodimethoxotungsten(VI)

$WF_4(OMe)_2$ (5.6 g, 17 mmoles) was heated to 80° for 19 hours, and yielded a blue-green liquid with some black solid.

The fraction volatile at -60° (0.3 g) was identified as Me_2O and SiF_4 (trace) (by i.r.[105, 103]).

The fraction volatile at 20° was a colourless liquid identified

as oxotetrafluoro(dimethyl ether)tungsten(VI), $WOF_4.OMe_2$ (2.2 g, 6.8 mmoles, yield 40%).

Anal. Found: C, 7.38; H, 1.90; F, 23.3; W, 56.5%. $C_2H_6F_4O_2W$ requires: C, 7.46; H, 1.88; F, 23.6; W, 57.1%. The ^{19}F n.m.r. spectrum (neat liquid, CCl_3F ref.) contained a major signal at -63.4 p.p.m. (single line, J_{WF}=67 Hz), and a weak signal (2% of total intensity) at -60.8 p.p.m. (doublet, J_{FF}=58 Hz) (cf. Table 1.3). The ^1H n.m.r. spectrum contained a major signal at 6.34 τ (single line), and a single line of less intensity (5% of total) at 6.52 τ assigned to Me_2O (6.76 τ [155]).

The residue (3.1 g), a blue-black solid, was not investigated.

(2) Trifluorotrimethoxotungsten(VI)

$WF_3(OMe)_3$ (7.2 g) was heated to 100°. Decomposition began after 30 minutes, and was complete after 12 hours.

The fraction volatile at -60° (1.7 g) was identified as a mixture of Me_2O, SiF_4, and MeF (trace) (by i.r. [105, 103]). The absorptions from MeF were largely obscured by those of Me_2O. Molecular weight: found, 56.4; Me_2O requires, 46.1; SiF_4 requires 104.1; MeF requires, 34.0.

The fraction volatile at 20° (0.2 g), a colourless liquid which hydrolysed rapidly in water to give WO_3, was not identified.

The involatile residue (5.3 g), a blue oil, was not investigated as extensive hydrolysis had occurred.

(3) Difluorotetramethoxotungsten(VI)

$WF_2(OMe)_4$ (6.9 g, 20 mmoles) melted ca. 80°; no decomposition occurred below 100°, but was complete after 18 hours at 145°.

The fraction volatile at -40° (1.9 g) was identified (by i.r.[105]) as Me_2O and MeF (trace) (1.9 g ≡ 41 mmoles Me_2O).

Molecular weight: found, 45.1; Me_2O requires, 46.1.

The involatile residue was a blue powder.

Anal. Found: C, 2.92; H, 0.86; F, 10.5; W, 67.1%; ratio W:F = 1:1.5.

Infrared spectrum (nujol mull, 1800 - 400 cm^{-1}) : 1550m, 1010m, 995m, 950 - 700sbr cm^{-1}.

(4) Tetrafluorodiethoxotungsten(VI)

It was not possible to perform the decomposition quantitatively, but a sample of $WF_4(OEt)_2$ heated to 50° (2.5 hours) turned black. The "molecular weight" of the fraction volatile at -40° was 49.8. EtF requires, 48.1. The infrared spectrum contained absorptions characteristic of SiF_4[103], but absorptions characteristic of EtF[177] were not well resolved.

Reactions followed by N.M.R. spectroscopy

(1) Tungsten hexafluoride and dimethyldimethoxysilane

From a reaction of WF_6 with a two-fold excess of $Me_2Si(OMe)_2$, a sample of the mixture was removed after 30 minutes. The ^{19}F and ^1H n.m.r. spectra (CCl_3F and T.M.S. ref.) contained signals

characteristic of Me_2SiF_2 ^{199} (^{19}F, multiplet, + 130.3 p.p.m.; ^{1}H, triplet, 9.68 τ, J_{HF}=7 Hz), cis-$WF_4(OMe)_2$ (^{19}F, two triplets, J_{FF}=65 Hz, of equal intensity at -64.0 and -45.4 p.p.m.; ^{1}H, multiplet, 4.65), cis- and trans-$WF_3(OMe)_3$ (^{19}F, singlet at -14.8 p.p.m., doublet-triplet, J_{FF}=62 Hz at -35.7 and-10.7 p.p.m. resp.; ^{1}H, multiplet, 5.0τ), and trans-$WF_2(OMe)_4$ (^{19}F, singlet at + 18.2 p.p.m.; ^{1}H, multiplet at 5.15τ). The latter signals were weak, and signals from cis-$WF_2(OMe)_4$ were not observed.

The n.m.r. tube was heated to 60° (15 hours) and the colour of the sample changed from colourless to blue. The signals from Me_2SiF_2 were unchanged, but no signals arising from $WF_{6-n}(OMe)_n$ species were observed. The ^{19}F n.m.r. spectrum contained signals at -60.8 p.p.m. (doublet, J_{FF}=55 Hz, characteristic of $W_2O_2F_9^-$, cf. Table 1.3) and -5.4 p.p.m. (broad multiplet, minimum of 4 lines). The ^{1}H n.m.r. spectrum contained signals at 4.98τ (multiplet), 5.64 τ (single line) and 6.44τ (single line).

(2) Isomerisation of tetrafluorodimethoxotungsten(VI)

A sample of cis-$WF_4(OMe)_2$ containing ca. 10% $WF_3(OMe)_3$ was set aside at 20° for 5 months. The colour became dark green and the ^{19}F and ^{1}H n.m.r. spectra did not contain signals characteristic of cis-$WF_4(OMe)_2$ and $WF_3(OMe)_3$. The ^{19}F n.m.r. spectrum (CCl_3F ref.) contained a major signal at -63.6 p.p.m. (single line, J_{WF}=68 Hz) characteristic of oxotetrafluoro(dimethyl ether)tungsten(VI),

$WOF_4.OMe_2$, and signals of less intensity (5%) at -60.9 p.p.m. (doublet, J_{FF}=59 Hz, J_{WF}=72 Hz) and + 144.9 p.p.m. (multiplet, minimum of 7 lines, J_{FF}=58 HZ) characteristic of $W_2O_2F_9^-$ (Table 1.3). The ^1H n.m.r. spectrum contained a major signal at 6.32 τ (single line) and signals of less intensity at 5.59τ (single line) and 4.91τ (multiplet).

CHAPTER FOUR

THE ^{19}F AND ^{183}W NUCLEAR MAGNETIC RESONANCE SPECTRA OF TUNGSTEN(VI) FLUORO-COMPLEXES

Introduction

This chapter presents a further discussion of the ^{19}F n.m.r. spectra and the stereochemistry of the tungsten(VI) fluoro-complexes prepared in this work. The ^{183}W chemical shifts of some of these complexes have been obtained by double resonance techniques in collaboration with Dr. Wm. McFarlane, Sir John Cass College, London.

Chemical Shifts

The frequency at which a magnetic nucleus absorbs energy when placed in a magnetic field is given by

$$\nu = H\gamma / 2\pi$$

where H is the magnetic field strength at the nucleus, and γ is the magnetogyric ratio of the nucleus. The great importance of the nuclear magnetic resonance phenomenon to the chemist stems from the fact that nuclear magnetic resonance frequencies are dependent to a small extent on the molecular environment of the nucleus. The applied magnetic field induces circulations of the electrons surrounding the magnetic nucleus

which is thereby shielded to some extent from the applied field. The shielding of a nucleus is the difference, H', between the effective magnetic field, H, at the nucleus, and the applied magnetic field, H_o, and is given by

$$H = H_o - H'$$
$$= (1 - \sigma) H_o \quad ,$$

where σ is a dimensionless number known as the shielding constant. The chemical shift difference, δ_{ij}, between two nuclei of the same isotopic species in environments i and j and with shielding constants σ_i and σ_j for the same applied field is

$$\delta_{ij} = \sigma_i - \sigma_j \quad .$$

For a particular isotopic species the magnitude of δ_{ij} depends on the atomic number. The observed range of ^1H chemical shifts is much smaller than that of ^{19}F chemical shifts. The chemical shift, δ, of a nucleus referred to an internal reference compound is given by

$$\delta = \sigma - \sigma_R = \frac{H - H_R}{H_R} \quad ,$$

where σ is the shielding constant of the nucleus, and σ_R is that of the reference compound.

Approximate calculations of the shielding constants for complex molecular systems have been made by dividing the shielding constants

into contributions from electrons localised on atoms and in chemical bonds. The induced current model[141] for calculating σ regards the shielding constant σ_A of nucleus A in a molecule as arising from induced electronic currents in the atoms and bonds, and, provided the electrons localised on atom A do not overlap appreciably with those on atom B, gives

$$\sigma_A = \sigma_{AA}^{dia} + \sigma_{AA}^{para} + \sum_{B \neq A} \sigma_{AB} + \sigma_A^{deloc} .$$

σ_{AA}^{dia} arises from induced diamagnetic currents on the atom A, and is dependent on the electron density around nucleus A, which, in turn, is dependent upon the electronegativities of the groups attached to A. σ_{AA}^{para} arises from induced paramagnetic currents on A, which result from the mixing of the ground and excited electronic states by the applied magnetic field. It has been shown that σ_{AA}^{para} is zero when the electrons localised on A are in pure S-states. σ_{AB} arises from local induced currents on the atoms in the molecule other than A, and may be positive or negative according to whether the induced currents are dimagnetic or paramagnetic in character. σ_A^{deloc} arises from induced currents involving delocalised electrons, and is particularly important in aromatic hydrocarbons.

When A is a hydrogen nucleus σ_{AA}^{para} is small compared with σ_{AA}^{dia}, since the p-character of the hydrogen bonding orbital is small, and ^{1}H chemical shifts are determined almost entirely by the diamagnetic

contribution arising from the magnetic field set up by the extranuclear electrons opposing the applied field. When A is a fluorine nucleus σ_{AA}^{para} is the dominant term. The importance of σ_{AA}^{para} in the treatment of ^{19}F chemical shifts arises from the presence of valency p-electrons in the fluorine atom, which, in a molecule, can depart considerably from spherical symmetry.

^{19}F Chemical shifts of Tungsten(VI) Fluoro-complexes

Figure 4.1 is a schematic diagram of the ^{19}F n.m.r. spectra of some of the tungsten(VI) fluorocomplexes prepared in this work. The spectral parameters for these compounds are listed in Table 4.1, and the chemical shifts are given relative to WF_6 using the relationship $\delta^{F}_{WF_6} = \delta^{F}_{CCl_3F} + 165$ p.p.m. Substitution of one or more of the fluorines of WF_6 by a less electronegative O-donor ligand results in a shift of the ^{19}F resonance to higher applied fields. The direction of this shift is that predicted by the theory of Saika and Slichter[200] which attributes ^{19}F chemical shifts mainly to changes in the paramagnetic contribution to nuclear screening. This contribution, which results in a shift to low field, should be zero for the spherically symmetrical fluoride ion, and large, i.e. inducing a greater shift to low field, in the fluorine molecule. In accord with this reasoning is the observation that the resonance of F_2 is 548 p.p.m. to low field of that of the fluoride ion.[201] It is expected, therefore, that there will be a shift to high field as the ionic character of the bond to

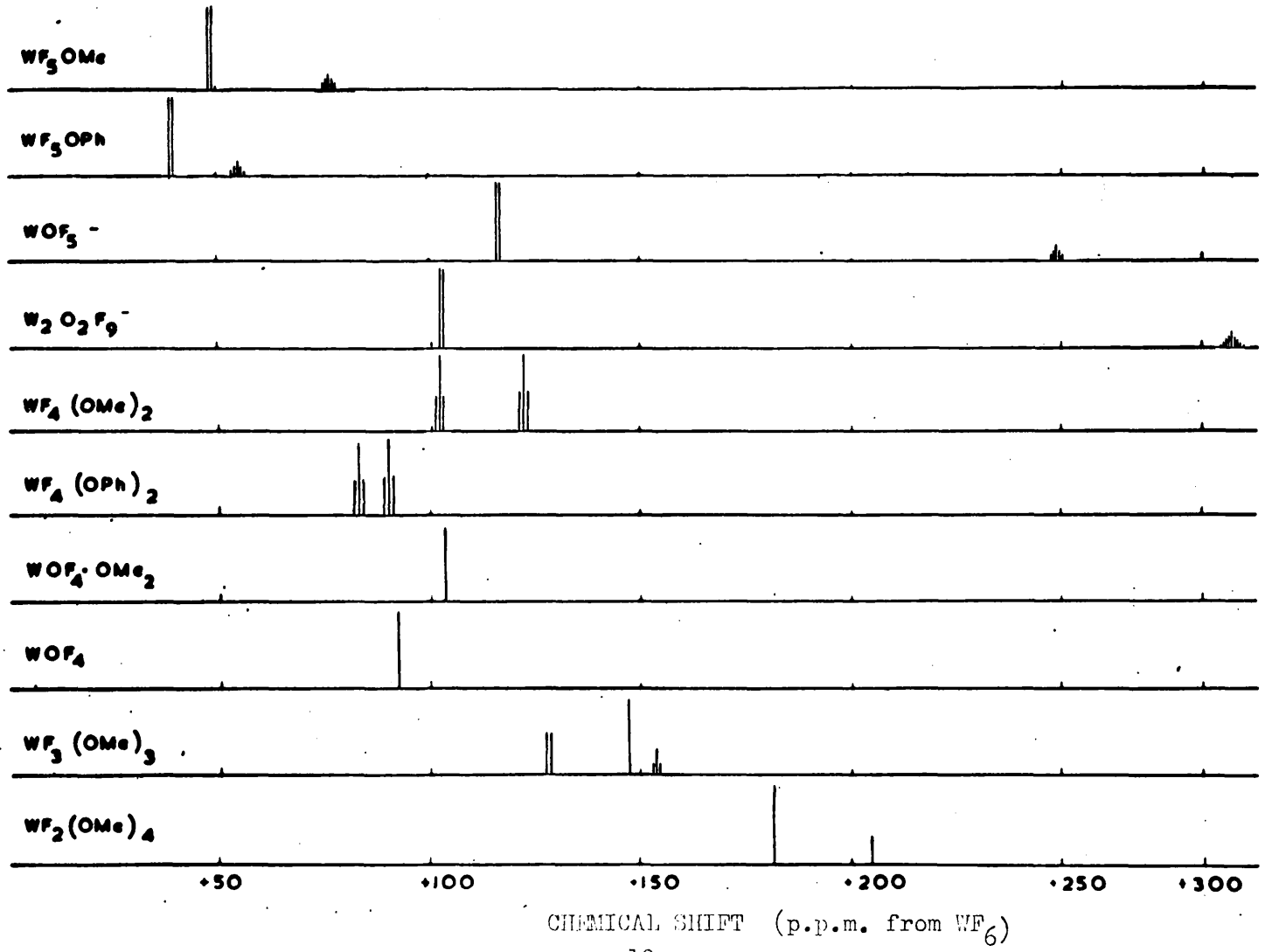


FIGURE 4.1: Schematic diagram of 56.4 MHz ^{19}F n.m.r. spectra of tungsten(VI) fluoro-complexes

TABLE 4.1

Complex	Solvent	^{19}F chemical shift[a] (p.p.m. from WF_6)[b] F_1	F_2	J_{FF} Hz	J_{WF} Hz	Ref.
WF_5OMe	C_6F_6	46	75	66	43(F_1) 33(F_2)	
cis-$WF_4(OMe)_2$	neat	101	121	66	46(F_1) 25(F_2)	
trans-$WF_3(OMe)_3$	C_6F_6	128	152	62		
cis-$WF_3(OMe)_3$	C_6F_6		146		18[c]	
trans-$WF_2(OMe)_4$	C_6F_6	182			14[c]	
cis-$WF_2(OMe)_4$	C_6F_6		204			
WF_5OPh	C_6F_6	39	53	65	39(F_1)	
cis-$WF_4(OPh)_2$	CH_3CN	81	89	68		
$(MeO)_3PMe^+WOF_5^-$	CD_3CN	115	249	52	70(F_1) 57(F_2)	
$W_2O_2F_9^-$	in $WOF_4.OMe_2$	105	311	58	71 51	
$WOF_4.OMe_2$	neat	102			68	
WOF_4	SO_2	91			64	35

[a] ± 1 p.p.m. [b] F_1 trans to F, F_2 trans to other ligand, where appropriate. [c] Incompletely resolved.

fluorine increases, i.e. as the electronegativity of the attached atom or group decreases. Correlations of the ^{19}F chemical shifts with the Pauling electronegativities of the heteroatoms have been successful for some binary fluorides.[201]

However, the direction of the shifts of the ^{19}F resonances of tungsten(VI) chlorofluorides (Table 4.2) and of the majority of substituted hexafluorostannates[190] on replacement of a fluorine by a less electronegative ligand is the reverse to that observed for the tungsten(VI) fluoro-complexes described above. Other factors must therefore influence the ^{19}F chemical shifts in these cases, and it has been suggested (e.g. ref. 190 and refs. therein) that these may include π-bonding, presence of low-lying excited states, and intramolecular field effects. In particular it has been suggested that intramolecular van der Waals interactions involving cis substituents may be important in determining the ^{19}F chemical shifts in $[SnF_{6-n}X_n]^{2-}$, (X = Cl, Br, I).[190]

In WF_5OR (R = Me, Ph), WOF_5^-, $W_2O_2F_9^-$ and trans-$WF_3(OMe)_3$ fluorine nuclei trans to fluorine (F_1) are less shielded than those trans to other ligands (F_2), and assignment of the ^{19}F resonances of cis-$WF_4(OR)_2$ (R = Me, Ph) and $WF_2(OMe)_4$ have been made on the reasonable assumption that the same situation obtains (chapters 2,3). This situation is also observed in tungsten(VI) chlorofluorides (Table 4.2) and in $ReOF_5$.[18] In the latter case the axial (i.e. F_2) and equatorial (i.e. F_1)

TABLE 4.2

^{19}F n.m.r. spectra of tungsten(VI) chlorofluorides.[38-40]

Complex	^{19}F chemical shift (p.p.m. from WF_6)[a] F_1	F_2	J_{FF} Hz	J_{WF} Hz
WF_5Cl	-16	+39	73	25
trans-WF_4Cl_2	-25			20
cis-WF_4Cl_2	-33	+30	66	
trans-WF_3Cl_3	-43	+27	62	
cis-WF_3Cl_3		+22		
trans-WF_2Cl_4	-54			
cis-WF_2Cl_4		+14		
$WFCl_5$		+8		

[a] F_1 trans to F, F_2 trans to Cl.

resonances are widely separated, and an explanation has been given in terms of fluorine-to-rhenium $p\pi$-$d\pi$ bonding.

There are three metal d-orbitals of proper symmetry for π-bonding in octahedral complexes.[202] In $ReOF_5$ it is supposed[18] that the presence of vacant 5d-orbitals on the rhenium atom encourages supplementation of the σ-bonding of the ligands by $p\pi$-$d\pi$ bonding, and that fluorine-to-rhenium π-bonding reduces the ionic character of the bond, thus causing the ^{19}F resonance to shift to lower field. The oxygen ligand in $ReOF_5$ is less electronegative than the fluorine ligands, and multiple bonding by the oxygen will considerably diminish the amount of multiple bonding by the axial fluorine as both ligands compete for the same metal d-orbitals. The equatorial fluorines, however, have access to a d-orbital not available to the oxygen. The axial Re-F bond is thus expected to be more polar than the equatorial Re-F bonds, and this can be correlated with the observation that the axial ^{19}F resonance is to high field of the equatorial resonance. Interestingly in IOF_5, where π-bonding is presumed to be absent, the axial and equatorial resonances are not widely separated, and the former is to lower field.

Although the ^{19}F chemical shifts of the fluoro-complexes in Figure 4.1 do not give any direct evidence of the presence of fluorine-to-tungsten $p\pi$-$d\pi$ bonding in the ground or excited states, it is possible to rationalise the variation in the chemical shifts by considering that the ability of the ligands to donate electrons to the tungsten t_{2g}

orbitals is in the order O > OMe > OPh > F. Thus an oxygen ligand produces a larger high field shift than OMe which, in turn, produces a larger high field shift than OPh, the effect being greater in the trans position. Explanations of the variation of ^{19}F chemical shifts in terms of π-bonding do not necessarily require additivity of substituent effects, and this may account for the fact that the relations between substituent effects and ^{19}F chemical shifts for $WF_{6-n}(OR)_n$ (Table 3.3) are only approximately linear.

^{19}F nuclei trans to other ligands in $[SnF_{6-n}(OMe)_n]^{2-}$, [190] TiF_4, 2D, [203] and $(TiF_5D)^-$ [204] (D = a neutral, monodentate, O donor ligand) are less shielded than those trans to fluorine, the reverse situation to that observed for the tungsten fluoro-complexes described above. Fluorine-to-metal π-bonding is unlikely to be of great importance in the fluorostannate complexes as the metal atom has a $4d^{10}$ configuration. Self-consistent arguments involving fluorine-to-metal π-bonding have been invoked to account for the ^{19}F chemical shifts of the titanium ($4d^0$) complexes. It is necessary in this case to postulate that fluorine-to-titanium π-bonding is greater than oxygen-to-titanium π-bonding from the ligands H_2O, ROH (R = Me, Et, ^iPr), substituted pyridine oxides, and substituted amides.

Stereochemistry of Tungsten(VI) Fluoro-complexes

Dyer and Ragsdale[205] have considered steric repulsion, symmetry effects and $p\pi$-$d\pi$ bonding as factors which might be expected to

influence the stereochemistry of $MF_4.2D$ (M = Ti, Sn) complexes in solution, and it is interesting to apply their arguments to the compounds $WF_4(OR)_2$ (R = Me, Et, Ph), $WOF_4.OMe_2$ and $WOF_4.OP(OMe)_2Me$. As the fluorine ligands are relatively small only the steric interactions between the other larger donors need be considered. Steric interference between two large donor molecules favours a trans configuration. The symmetry of a trans-$MF_4.2D$ complex is higher than that of a cis-$MF_4.2D$ complex, and entropy considerations lead to the conclusion that a cis configuration is favoured as the temperature is increased. Ligands capable of π-bonding will compete for the available metal d-orbitals, and this also favours a cis configuration. For $TiF_4.2D$ complexes (e.g. where D is a substituted pyridine oxide) it is concluded that a trans configuration is adopted only when there is sufficient steric interaction to overcome symmetry effects and the tendency to maximise π-bonding.

Steric considerations are not likely to be of great importance in the complexes $WF_4(OR)_2$, (R = Me, Et, Ph) $WOF_4.OMe_2$ and $WOF_4.OP(OMe)_2Me$. The preferred cis configuration of $WF_4(OR)_2$ can be rationalised on the basis that (OR) is a better π-donor than fluorine. It is interesting that both cis and trans isomers of WF_4Cl_2 have been observed, and that the ^{19}F chemical shifts of the tungsten chlorofluorides suggest that π-bonding may be less important than in the complexes with O-donor ligands. The trans configurations of $WOF_4.OMe_2$ and $WOF_4.OP(OMe)_2Me$

can be explained in terms of π-bonding if the order of the π-bonding ability of the ligands is taken as $O > F > Me_2O$, $(MeO)_2P(O)Me$.

It has been suggested[206] that oxygen-to-metal π-bonding favours a cis configuration for d^0 trioxo-species, and it is noteworthy that the cis/trans ratio for $WF_3(OMe)_3$ is 2:1 (chapter 3). The cis/trans ratio for $WF_2(OMe)_4$ is 1:3, and this is less easily rationalised as π-bonding considerations in d^0 tetraoxo-species are said to favour the cis configuration.[206]

It must be noted, however, that discussions of the preferred stereochemistry of $WOF_4.OMe_2$, $WOF_4.OP(OMe)_2Me$ and $WF_2(OMe)_4$ are subject to a measure of uncertainty as the structures of these complexes have been assigned on the basis of single line ^{19}F resonances.

^{183}W Chemical Shifts

Heteronuclear magnetic double resonance has been used to determine chemical shifts which cannot be conveniently obtained by single resonance methods. The technique has been recently reviewed by McFarlane.[207] If the nucleus of interest is spin coupled to a ^1H or ^{19}F nucleus, it is possible to use the inherent sensitivities and favourable relaxation times of the latter to obtain the heteronuclear parameters. The method consists of observing the ^1H or ^{19}F n.m.r. spectrum of the compound and simultaneously irradiating at the resonant frequency of the nucleus under investigation. From the perturbation or disappearance of spin-spin coupling on application of the appropriate

second frequency, the chemical shift of the nucleus of interest can be obtained. The chemical shifts of the ^{183}W nuclei ($I = \frac{1}{2}$, natural abundance 14.28%) in the compounds listed in Table 4.3 were obtained from double resonance experiments on their ^{19}F n.m.r. spectra.

In common with other heavy nuclei[141] the ^{183}W chemical shifts are very substantial and the technique is of potential value for studying these systems. In heteronuclear double resonance experiments these large chemical shifts may involve a lengthy initial search procedure, particularly for nuclei for which accurate values of the magnetogyric ratios are not known. Solvent effects for heavier nuclei are large, and measurement of chemical shifts to closer than 1 p.p.m. is probably unwarranted. It is interesting that the ^{183}W resonance of the coloured solution of WF_6 in benzene is 10 p.p.m. downfield from that of WF_6 in cyclo-C_5H_{10}. This technique may provide a sensitive tool for the investigation of weak donor-acceptor complexes of WF_6 (cf. chapter 1).

The data in Table 4.3 have provided some confirmation of the formulation of some of the complexes prepared in this work. The similarity of the ^{183}W chemical shift of the compound formulated as $WOF_4 \cdot OS(OMe)_2$ (chapter 2) to those of $WOF_4 \cdot OP(OMe)_2Me$ and $WOF_4 \cdot OMe_2$ lends weight to previous assignments, and the similarity of the ^{183}W chemical shifts of WOF_5^- and $W_2O_2F_9^-$ is expected.

The ^{183}W resonances are all to low field of WF_6, and those of the

TABLE 4.3

^{183}W chemical shifts of some tungsten(VI) fluoro-complexes

Compound	Solvent	^{183}W Chemical Shift (p.p.m. from neat WF_6)	J Hz	Ref.
WF_6	cyclo C_5H_{10}	-11 [a]		82
WF_6	C_6H_6	-21 [a]		82
WF_5OMe	C_6F_6	-40		
cis-$WF_4(OMe)_2$	neat	-160		
WF_5OPh	C_6F_6	-190		
cis-$WF_4(OPh)_2$	CH_3CN	-257		
$WOF_4 \cdot OMe_2$	neat	-565		
$WOF_4 \cdot OP(OMe)_2Me$	CD_3CN [b]	-533	$J_{WP} = 4.5 \pm 0.2$	
$WOF_4 \cdot OS(OMe)_2$ (?)	$(MeO)_2SO$	-529		
$(MeO)_3PMe^+WOF_5^-$	CD_3CN [b]	-605		
$W_2O_2F_9^-$	$(MeO)_2SO$	-617		
WF_5Cl		-665		208
trans-WF_4Cl_2		-1235		208
cis-WF_4Cl_2		-1335		208

[a] Assuming negligible ^{19}F chemical shift change. [b] A ^{31}P double resonance experiment on the ^1H spectrum confirmed the presence of (i) free $(MeO)_2P(O)Me$ (ii) coordinated $(MeO)_2P(O)Me$ and (iii) $(MeO)_3PMe^+$.

fluoro-complexes with O-donor ligands are in the opposite direction to their ^{19}F chemical shifts. A Saika-Slichter type correlation of the ^{183}W chemical shifts with the electronegativities of the substituents is inadequate, and clearly other factors are involved.

Conclusions

The ^{19}F chemical shifts and the stereochemistry of the tungsten(VI) fluorocomplexes prepared in the present work can, in general, be explained in terms of the varying abilities of the ligands to engage in ligand-to-metal π-bonding. However, there is no direct evidence of such π-bonding. A simple explanation cannot be forwarded to account for the ^{183}W chemical shifts of the complexes.

Experimental

The ^{183}W chemical shifts were obtained by Dr. Wm. McFarlane using a modified JEOL-C-60-H spectrometer operating at 56.45MHZ.

APPENDIX

Apparatus and Instrumentation

Standard vacuum techniques were used throughout, and rigorous precautions were taken to exclude moisture from all systems. A vacuum line was constructed from short Pyrex-glass manifolds, and was designed to enable the separation of mixtures of volatile compounds, the determination of molecular weights by the vapour density method, and the preparation of samples for gas infrared spectroscopy and liquid n.m.r. spectroscopy. Standard ground glass joints greased or waxed with Apiezon or polychlorofluorocarbon (MCM or Dupont) products, magnetic breakseals, and Teflon,glass stop-cocks (Fisher Porter Co., Ace Glass Inc., Quickfit "Rotaflo") were used where required. It was necessary to compromise between an all-glass system affording a higher vacuum and a system which could be easily dismantled for cleaning after a reaction. All glassware was "flamed out" under vacuum before use, and with a rotary oil pump and a mercury diffusion pump in series a vacuum of 10^{-4} mm or better could be obtained. Involatile compounds were handled in a dry-box using P_2O_5 as dessicant.

Reaction vessels were of Pyrex-glass (volume ca. 25 ml), and were fitted with Teflon,glass stop-cocks or magnetic breakseals. N.m.r. and sample tubes were attached to sidearms when required for involatile products.

Typical glass reaction vessels are shown in Figures 1 and 2.

Metal vessels were of stainless-steel (Hoke) or Monel-metal (home made), and were fitted with Hoke needle valves and Swagelok couplings. Metal cones were made to fit into standard ground glass joints. These vessels (volume ca. 25 ml) were used for reactions involving high temperatures and pressures.

Infrared spectra of gases were taken in 5 or 10 cm gas cells with KBr windows, and pressures were measured with a mercury manometer. Solid samples were run as nujol or florube mulls using NaCl, AgCl, KBr and CsI plates as appropriate or as Rigidex discs. The following instruments were used according to the range required: Perkin-Elmer 225, 237, 257 and 457; Unicam SP. 100 and SP. 200; FS. 720 RIC Interferometer.

N.M.R. Spectra were obtained using a Perkin-Elmer R.10 spectrometer operating at 60.00 MHz for ^{1}H and 56.46 MHz for ^{19}F, with a probe temperature of 33.5°. Volatile samples were distilled into pyrex tubes sealed to the vacuum line. Involatile samples were also prepared under vacuum by tipping a portion into an n.m.r. tube attached to a glass vessel. (Figure 1). Solvents and internal references were distilled into the sample tubes under vacuum. Fluorine spectra were measured in p.p.m. relative to trichlorofluoromethane, CCl_3F, and proton spectra were referenced with tetramethylsilane (T.M.S.), $(CH_3)_4Si$. (^{1}H chemical shifts are expressed as τ (tau) values throughout).

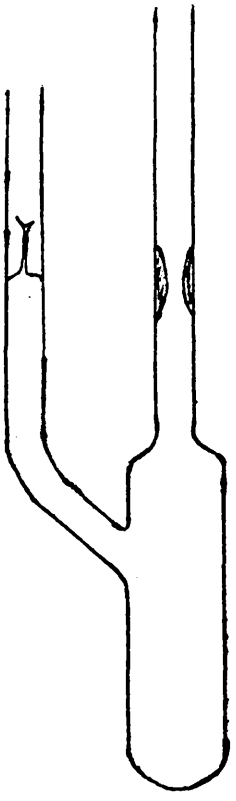


Figure 2 :
Breakseal flask.

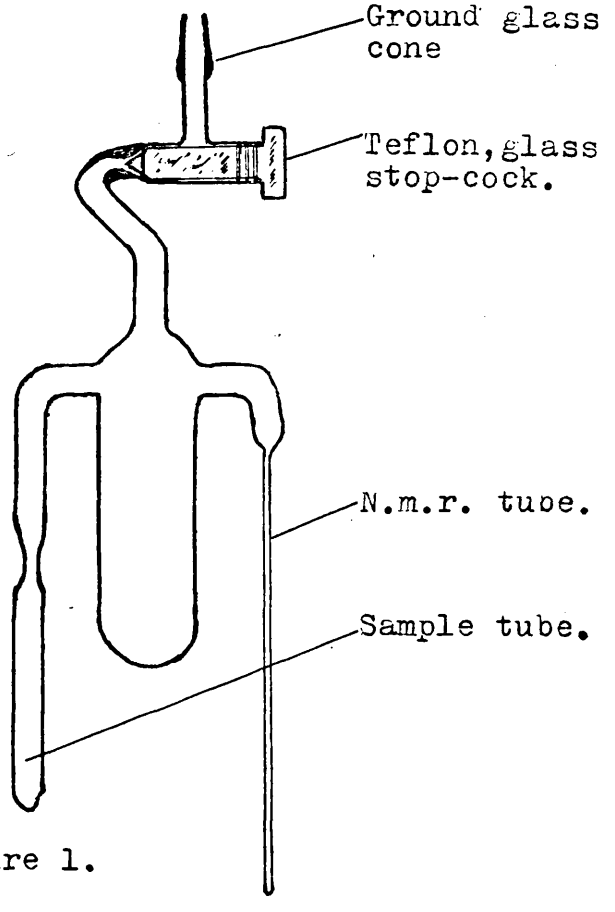


Figure 1.

Mass spectra were recorded at 70 e.V. using A.E.I. M.S.9 and A.E.I. M.S.12 spectrometers.

Ultra-violet spectra were recorded on Unicam SP 800 and Beckmann D.K.-2A instruments.

Elemental Analyses. Tungsten was determined gravimetrically as WO_3, using cinchonine hydrochloride to facilitate precipitation. Analyses for other elements were performed by Beller (Göttingen, W. Germany) Bernhardt (Muhlheim, W. Germany) and Yarsley (Surrey, England).

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